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PREFACE

The name of Dr. C. R. Reddy is well known to scholars and educationists both in India and abroad. The articles that were presented to him by scientists from different parts of India on the occasion of his *ṣaṣṭyabdapūrti* in December 1940, are now published in a collected form as Ramalinga Reddy *Ṣaṣṭyabdapūrti* Commemoration Volume: Part I—Sciences. The sale proceeds will be utilized for the benefit of the Andhra University of which Dr. Reddy is the Vice-Chancellor. The thanks of the Publication Committee are due in the first place to the contributors for their valuable articles, and secondly to the Superintendent, Baptist Mission Press, Calcutta, for his patience and courtesy in dealing with the difficulties of printing a work of this character. In compliance with Dr. Reddy's desire that there should be no eulogistic references to him in the Commemoration Volume, the Committee are obliged to content themselves with inserting only a brief biographical notice in the Preface.

CATTAMANCHI RAMALINGA REDDY, born December 10, 1880, in Chittoor District, Madras. Educated at (i) High School, Chittoor, (ii) Christian College, Madras, and (iii) St. John's College, Cambridge, where he was a Foundation Scholar. Graduated B.A. in Philosophy and History from Madras University, 1901. Took a first in History Tripos at Cambridge University, 1905. Vice-President of Cambridge Union Society, and Secretary of Cambridge University Liberal Club, 1905. Travelled in Germany, France, Canada, America, China, Japan and the Philippines for study of educational organizations, systems of local self-government, and state methods of promoting industry and commerce, in those countries. Vice-Principal of Maharaja's College, Baroda, 1908. Principal of Maharaja's College, Mysore, 1916-18. Inspector-General of Education, Mysore, 1918-21. Member of All-India Advisory Board of Education, 1921. Elected by Madras University to the 1st and 2nd Legislative Councils. Vice-Chancellor of Andhra University, 1926-30, and since 1936. President of Inter-University Board of India, 1937. Awarded D.Litt. *honoris causa* by Andhra University, 1937. Nominated to Upper Chamber of New Provincial Legislature. Publications:—Lectures on University Reform, Political Economy (in Telugu), Kavivatattvavicāramu (in Telugu), Vyāsamañjarī (in Telugu), Deputation Studies in 2 vols.

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THE TWO TYPES OF X-RAY REFLECTION IN CRYSTALS ¹

By

C. V. RAMAN and N. S. NAGENDRA NATH

1. *Introduction*

One of the most remarkable and fruitful discoveries in modern science was made when Max von Laue applied the principles of the wave-theory to find the effect of passage of a pencil of X-rays through a crystalline plate and arrived at conclusions which were strikingly confirmed by experiment. When the pencil after traversing the crystal is received on a photographic plate, we find recorded on the plate, as predicted by Laue, numerous spots in geometric array, their positions being closely related to the internal atomic architecture of the crystal and the direction of passage of the incident X-rays. The location of the spots in the Laue pattern is determined by the consideration that the secondary radiations from the atoms in the crystal co-operate in the directions indicated by the spots by reason of an agreement in phase, such agreement being itself a consequence of the arrangement of the atoms in a regular space-lattice. The Laue conditions which express this situation are mathematically equivalent to the Bragg formula; the latter follows very simply from the consideration that the crystal is a regularly stratified medium and should, therefore, selectively reflect the radiations falling on its strata at an angle of incidence appropriate to their spacing and to the wave-length of the X-rays in accordance with a general principle familiar to students of optics.

¹ The new type of X-ray reflection forming the subject of this paper was first described and an explanation of it on the basis of the quantum theory was first given in a series of papers published early last year (1940) by Raman and Nilakantan. The present report is intended to be a self-contained theoretical exposition of the subject and incorporates the ideas expounded in the papers by Raman and Nilakantan, as also the fuller mathematical treatment given by Raman and Nath and published in July, 1940. Recent experiments by Nilakantan with diamond have completely established the quantum theoretical explanation of the phenomenon.

Laue's discovery was a vindication of the wave-theory and was naturally regarded as finally settling the issue, then being keenly debated, whether X-rays were corpuscles or waves, in favour of the latter hypothesis. Actually, however, the position is not quite as simple as this. As we know at the present time, there is an essential duality in the behaviour of the fundamental physical entities. They have a wave aspect as well as a particle aspect, and these two characters are complementary and not contradictory. To get a complete picture of the observable phenomena, therefore, we can ignore neither one aspect nor the other. It is thus necessary to bear in mind the particle aspect as well as the wave aspect of the Laue phenomenon, and indeed, when we approach the subject from this point of view, the possibility of there being two distinct kinds of X-ray reflection becomes apparent. From the particle point of view, the X-ray reflections of the Laue type are *elastic* collisions of the photon with the crystal lattice, while from the wave point of view, they arise from the fact that the crystal has a static periodicity of structure. This suggests that a second type of X-ray reflection in crystals should be possible which, from the particle standpoint, is an *inelastic* collision in which the photon gives up a part of its energy during the encounter and excites the vibrations of the crystal lattice, while from the wave standpoint, the reflection is due to the *dynamic stratifications of density* arising from such vibrations of the lattice. From either point of view, a change of frequency is seen to be a necessary feature of the second type of X-ray reflection; we may therefore refer to it as the quantum or modified reflection to distinguish it from the classical or unmodified reflections.

2. *Theory of Modified Reflection*

We may now proceed to consider a little more closely the mechanism of the modified X-ray reflection and its relation to the structure of the crystal. The classical or unmodified X-ray reflections arise from the fact that the electron density in the crystal is a periodic function of the co-ordinates in three dimensions. The intensity of the reflection by any particular set of crystal planes is determined by a quantity known as its structure amplitude which

specifies the variation of the mean electron density over a plane when such plane is moved normally to itself through the crystal. The positions occupied by the atoms in the unit cell of the lattice are the most important factor in determining the structure amplitudes, though other factors such as the number of electrons and the distribution of electron density in each atom also enter into it.

With scarcely an exception, the actual crystals with which we are concerned contain more than one atom per unit cell, indeed usually several atoms of the same or of a different kind. These atoms are held together in their places as the result of forces acting between each atom and its neighbours. Each individual atom is capable of vibrating about its position of equilibrium, but in view of the existence of interatomic forces, it is more appropriate to consider the crystal lattice as a whole and to fix our attention on some one or another of its possible modes of vibration. These modes fall into two divisions, namely, the vibrations of the acoustic type and those of the optical type. The vibrations of the acoustic class lie for the greater part in the lower ranges of frequency, while the optical vibrations have frequencies falling in the infra-red region of the spectrum. The character of the movements involved in these two classes differs essentially. The acoustic vibrations consist chiefly of translatory movements of the unit cells of the lattice relative to each other, while in the vibrations of the optical class the atoms within each unit cell oscillate relatively to each other about their common centre of gravity. The interatomic displacements within the unit cells for the acoustic vibrations and the translations of the unit cells for the optical vibrations are in each case of relatively minor importance.

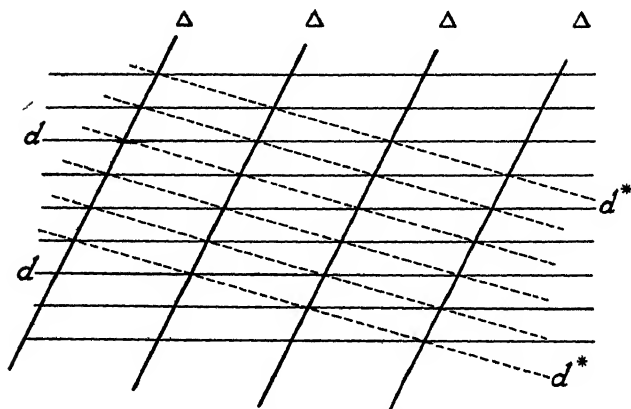
We may now fix our attention on the optical vibrations of the crystal lattice and consider their effect on the structure amplitudes responsible for the X-ray reflections. In the first instance, we may make the simplifying assumption that the oscillation in all the unit cells is of the same frequency, amplitude and phase. It is evident that with this restriction, the atomic vibrations do not affect the uniformity of the crystal structure; the spacing and orientations of the crystal planes remain completely unaltered. The structure

amplitudes of the crystal, however, alter periodically with time to an extent depending on the magnitudes and directions of the atomic displacements of which only the components normal to the spacing under consideration are effective. It is evident that the electronic density in the crystal would, in these circumstances, exhibit two different kinds of space variation, a static structure amplitude which is not a function of time, and a dynamic structure amplitude which varies with time and has the same frequency as the optical vibration of the crystal lattice. If the vibration of the lattice is sufficiently intense, the existence of a dynamic structure amplitude should evidently result in an alteration of the static structure amplitude, in most cases making it smaller than what it would be in the absence of such vibration.

From optical theory, it is evident that a dynamic structure amplitude would result in sharply defined monochromatic reflections in the same way as a static structure amplitude, except that the reflections would now occur with a change of frequency. Since under the assumptions made, the dynamic structure amplitudes do not differ from the static ones in respect of their spacings and orientations, the geometric conditions necessary for the observation of the static and dynamic reflections would also be identical, in other words, these reflections would either appear or not appear together in the same circumstances. If, for instance, the incident X-radiation be monochromatic, neither the modified nor the unmodified reflection would be observable unless the Bragg condition is satisfied.

3. *Geometric Law of Modified Reflection*

We may now remove the restrictive assumption made that the atomic oscillations occur in identically the same phase in all the unit cells comprising the crystal. The oscillation will be assumed to have the same frequency and amplitude everywhere, but its phase will be regarded as variable from cell to cell. While this variation of phase would not affect the *static structure amplitudes* giving the unmodified reflections, it would profoundly influence the *dynamic structure amplitudes* and the effects produced by them. This is very readily seen from the diagram given below, in which



Graphical Derivation of Dynamic Spacings.

the thin lines represent a set of crystal planes and, therefore, also the planes along which the time-variations of electron density would be the same, if the phase of the atomic vibrations were everywhere identical. The heavy lines crossing these at any angle represent the planes along which the phase of the atomic vibrations is constant. It is then evident that the dynamic stratifications of electron density would be along the diagonal planes cutting through the crystal spacings and the phase wave-fronts of the atomic vibration. These diagonal planes are indicated by the dotted lines in the figure, and their spacing and orientation are given by the vectorial formula

$$\frac{\vec{1}}{d^*} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \quad \dots \quad \dots \quad \dots \quad (1)$$

Here d^* is the spacing of the dynamic stratifications of electron density, d is the static crystal spacing, and Δ is the spacing of the phase-waves of the atomic vibration in the crystal lattice. Equation (1) shows that in the limiting case when Δ is infinite, d^* becomes identical with d both in magnitude and direction. The classical and quantum reflections then coincide as already remarked.

So far as the optics of the cases is concerned, the classical and quantum reflections are on a similar footing. For the former to occur, the Bragg condition, namely

$$2d \sin \theta = n\lambda \quad \dots \quad \dots \quad \dots \quad (2)$$

must be satisfied, while for the quantum reflections, it is similarly necessary that

$$2d^* \sin \psi = n\lambda \quad \dots \quad \dots \quad \dots \quad (3)$$

θ and ψ being the glancing angles of the incident beam on the static and dynamic stratifications measured in the respective planes of incidence. Denoting by ϑ and ε , the angles which the crystal planes make respectively with the phase-waves and with the dynamic stratifications, we have from equation (1) and the figure,

$$d^* \sin \vartheta = d \sin (\vartheta + \varepsilon) = \Delta \sin \varepsilon. \quad \dots \quad \dots \quad (4)$$

Substituting the first of these relations in (3), we obtain

$$2d \sin \psi \sin (\vartheta + \varepsilon) = n\lambda \sin \vartheta. \quad \dots \quad \dots \quad (5)$$

From equation (4), we see that if the wave-length Δ is large compared with the crystal spacing d or the dynamic stratification d^* , the angle ε would be small compared with ϑ or $(\vartheta + \varepsilon)$. Hence, provided ϑ is not nearly equal to 0 or π , we may write (5) in the *approximate* form

$$2d \sin \psi = n\lambda \quad \dots \quad \dots \quad \dots \quad (6)$$

which, it will be seen, is merely (3) with d written for d^* , that is to say, with the spacing of the dynamic stratifications put equal to that of the crystal planes from which they are derived. *Equation (6) is the same as equation (2) with ψ written for θ and is thus the geometric law for quantum reflections analogous to the Bragg law for the classical reflections.* Since the angular separation between the incident beam and the quantum reflection is 2ψ , equation (6) indicates that within the limits of its validity, *the angular separation of the quantum reflection and the incident beam is independent of the setting of the crystal and is equal to the angular separation of the classical reflection from the incident beam at the Bragg setting of the crystal.*

If Δ is infinite, it follows from (4) that $\varepsilon = 0$ and the approximate equation (6) becomes identical with the rigorous equation (5). How nearly this continues to be true when ε is finite depends on the angle ϑ . If $\vartheta = \pi/2$, $\sin \vartheta = 1$ and differs little from $\sin (\vartheta + \varepsilon)$ even when ε is as much as $\pm 10^\circ$. Hence, *for the particular case in which the phase wave-fronts are transverse to the crystal planes, the simple formula (6) may be regarded*

as *practically the rigorous geometric law of quantum reflection*. If, however, the inclination ϑ of the phase wave-fronts to the crystal planes is much less than $\pi/2$, it is not permissible to write $\sin \vartheta = \sin (\vartheta + \varepsilon)$ except for very small values of ε , and hence in such a case, the rigorous formula (5) should be employed. It is evident that the angular separation 2ψ of the quantum reflection from the incident beam would not then be independent of the crystal setting, but would be greater or less than the fixed value given by equation (6) according as ε is negative or positive, that is to say, according as the tilt of the dynamic stratifications with respect to the crystal planes is one way or the other.

The static and dynamic reflecting planes are coincident when Δ is infinite and ε is, therefore, zero. The planes of incidence for both reflections are, therefore, identical in this particular case. If this result be true generally, *it would follow that the quantum reflection by any particular crystal spacing appears in the same plane of incidence as the usual Laue reflection*. We may then write $2\psi = (\varphi + \theta)$ and $2\varepsilon = (\varphi - \theta)$, φ being the glancing angle of the quantum reflection measured with reference to the crystal planes. Equation (5) then becomes

$$2d \sin \frac{\varphi + \theta}{2} \sin \left(\vartheta + \frac{\varphi - \theta}{2} \right) = n\lambda \sin \vartheta \quad \dots \quad (7)$$

while equation (6) takes the form

$$2d \sin \frac{1}{2}(\varphi + \theta) = n\lambda \dots \dots \dots (8)$$

It is easily seen that the rigorous formula (7) would in every case give values of φ closer to θ than the approximate formula (8), the difference being least when $\vartheta = \pi/2$. In general, therefore, when ϑ is less than $\pi/2$, *the quantum reflection is nearer the Laue reflection than the fixed position indicated by the approximate formula; it moves in the same direction as the Laue spot, though much more slowly, as the crystal is rotated; it coincides with and is overtaken by the Laue spot at the Bragg setting and continues to follow its further movement as the crystal is turned away from that setting*. In the limiting case when $\vartheta = 0$, equation (7) indicates that $\varphi = \theta$, in other words, the quantum reflection appears superposed on the Laue spot.

4. *Intensity of Modified Reflection*

The modified reflection is the result of the crystal taking up a quantum of energy $h\nu^*$ and the photon going off with the remainder of the energy $h(\nu - \nu^*)$, ν and ν^* being the frequency of the incident radiation and of the lattice vibrations respectively. The energy $h\nu^*$ being shared by all the lattice cells in the crystal, the amplitude of vibration and the resulting dynamic structure amplitude would be exceedingly small. It might, therefore, seem at first sight that the probability of the process occurring would be negligible. Actually, however, the small probability of the individual process is set off by the fact that the number of lattice cells N in the crystal is enormously large, and the system, therefore, possesses N discrete frequencies of vibration ranging around the value ν^* . The fraction dN/N of this large number which becomes effective in any particular circumstances determines the observed intensity of the quantum reflection. This fraction should clearly be a function of the magnitude and direction of the phase vector $1/\Delta$ which we shall denote for convenience by the symbol δ . We may, therefore, write

$$dN/N = \frac{1}{4\pi} G(\delta, \chi, \vartheta) \sin \vartheta \, d\vartheta \, d\chi \, d\delta \quad \dots \quad (9)$$

In this equation, ϑ is the angle already introduced, namely the inclination of the phase wave-fronts to the crystal strata. χ is the azimuth of a plane normal both to the crystal strata and to the phase wave-fronts, the reference plane for which $\chi = 0$ being the plane of incidence on the crystal strata. $\sin \vartheta \, d\vartheta \, d\chi$ is, therefore, the elementary solid angle within which the vector δ lies.

The dependence of the G -function upon the value of δ should evidently be very pronounced. Since the characteristic frequency ν^* corresponds to a zero value of δ , we may expect the possible degrees of freedom to cluster densely around small values of δ and to thin out for large values of δ . In other words, the G -function would have a strongly marked maximum when $\delta = 0$ and diminish rapidly as δ increases. If, therefore, we regard the other variables in the function as having fixed values, e.g. $\chi = 0$ and $\vartheta = \pi/2$, the variation of intensity of the quantum reflection would depend

solely on the value of δ determined by the angles of incidence and reflection. It would then follow from equation (1) that *the intensity of the quantum reflection would be a maximum at the Bragg setting of the crystal for which $\varphi = \theta$ and would fall off rapidly as the crystal is moved away from this setting in either direction.*

It will be noticed that we have written the G-function with the angles χ and ϑ appearing explicitly in it, thereby indicating that the number of degrees of freedom lying between given limits of δ depends on the inclination of the wave-fronts to the crystal planes and also on the azimuth of the plane which is normal to both the static and dynamic stratifications of density. Such a dependence is to be expected on dynamical grounds. It is well known that in a crystal, the relation between wave-length and frequency for vibrations of the *acoustic class* is a function both of the direction of vibration and the direction of propagation, the wave-front splitting up into a surface of three sheets even in a cubic crystal. There would, therefore, be no justification for assuming that for vibrations of the optical class, the distribution of the degrees of freedom would be independent of either the orientation of the wave-fronts in the crystal, or of the directions of the atomic vibration in them. In our present problem, we are concerned with the modes of vibration in which the displacements of the atoms are predominantly normal to the particular crystal planes under study, since displacements parallel to the planes have no effect on their structure amplitudes. We may, therefore, reasonably anticipate that the G-function should show a strongly marked dependence on the angles ϑ and χ which enter in our problem.

It is evident that if the angles ϑ , χ defining the orientation of the phase-waves are regarded as entirely arbitrary, the optical conditions necessary for a reflection of the X-rays would be insufficient to indicate a unique direction for such reflection for any given setting of the crystal. It is, however, easily shown analytically or geometrically that they suffice to indicate a direction which would correspond to a minimum value of δ and therefore also to a maximum observable intensity of reflection, the values of χ and ϑ corresponding to such direction being 0 and $(\pi/2 - \varphi)$ respectively. The zero value

of χ indicates that the reflection would be in the plane of incidence, while the value $(\pi/2 - \varphi)$ on substitution for ϑ in (7) yields the formula

$$d \sin (\varphi + \theta) = n\lambda \cos \varphi \quad \dots \quad (10)$$

which may also be written as

$$d (\sin \theta + \cos \theta \tan \varphi) = n\lambda \quad \dots \quad (11)$$

both reducing to the Bragg formula when $\theta = \varphi$.

The considerations on which equation (11) is based would, however, be invalid and the results given by this formula would be contradicted by experiment, if the angles χ and ϑ appear explicitly in the distribution function $G(\delta, \chi, \vartheta)$ as assumed in our equation (9). For, when this is the case, the maximum of this function would be determined, not solely by the variations of δ , but also by the independent variations of χ and ϑ , and the preferred values of these angles which make the G -function a maximum must, therefore, influence both the intensity of the modified reflection as well as the plane and direction in which it is observed. The value of χ determines the plane of reflection, while that of ϑ notably influences the direction of reflection in that plane. Hence, the more precisely these angles can be specified, the more sharply defined would the direction of reflection be. The dependence of the distribution function on the angle variables thus plays an important part in determining all the observable features of the quantum reflection, namely the plane and the direction in which it is to be found, its sharpness and its intensity. The preferred value of ϑ is in particular of special importance and may be expected to depend on the substance chosen for investigation and possibly even on the particular set of crystal planes from which the reflections are observed. It may be evaluated by observing the quantum reflections over a sufficiently wide range of settings of the crystal and comparing the experimental results with the general formula (5) or its near equivalent (7).

5. Effect of Acoustic Vibrations

We may now briefly discuss the phenomena resulting from the excitation of those crystal vibrations which lie in the acoustic

range of frequency. When the number of atoms in the unit cell of the lattice is fairly large, the proportion of the aggregate number of degrees of freedom appearing as acoustic vibrations is small and the effects due to them are of small importance compared with those arising from the optical vibrations. Nevertheless, they deserve some consideration. The distinguishing feature of the acoustic vibrations is that they involve translatory movements of the unit cells, in other words a disordering of the crystal lattice, while the optical vibrations involve such movements to a negligible extent and may, therefore, be excited without distorting the crystal lattice. We have already noticed the latter as the special feature which enables the crystal to give modified or quantum reflections. We shall presently see that no such reflections would result from crystal vibrations of the acoustic class, and that on the contrary these vibrations would give rise only to a diffuse scattering of the X-rays.

A longitudinal sound-wave causes the mean electronic density in a crystal to vary periodically, and if its wave-length is sufficiently large in relation to the spacing of the lattice planes, we may ignore the latter and regard the wave itself as a time-periodic stratification of electronic density. Accordingly, the X-ray photon impinging on the crystal should excite such sound waves by inelastic collision and itself be reflected in the process, provided that the length Δ of the sound-wave, the glancing angle θ on its wave-fronts and the X-ray wave-length λ satisfy the relation

$$2\Delta \sin \theta = \lambda. \quad \dots \quad (12)$$

Accordingly, since both Δ and θ are arbitrary, the effect here contemplated would give rise to a diffuse scattering in directions surrounding the incident beam and lying within a cone of semi-vertical angle 2θ determined by the limiting value of Δ at which the argument fails, namely, when Δ is of the same order of magnitude as the lattice spacings in the crystal.

To find the phenomena in directions lying outside this cone, the procedure to be followed would be formally analogous to that indicated earlier for the optical vibrations, namely, to analyze the structure amplitudes of the crystal into a static part and a dynamic part having the frequency of the acoustic vibration, and

to consider the effect of the latter separately. The detailed results would, however, be quite different from those obtained for the optical vibrations. While an infinite wave-length Δ for the optical vibrations corresponds to one or other of the characteristic frequencies at which there is a maximum concentration of the degrees of freedom of the system, we have exactly the opposite situation in the acoustic case, the infinite wave-length then corresponding to zero frequency and a minimum concentration of the degrees of freedom. Hence the arguments which indicate that in the optical case the reflected beam is limited to particular directions in the plane of incidence are wholly inapplicable for the acoustic vibrations.

We conclude that *the acoustic vibrations of the crystal lattice, though they may be excited by an inelastic collision of the photon, give rise to a diffuse scattering without any pronounced directional effects.*

6. Analogy with Light Scattering

As is well known, when monochromatic light traverses a crystal and the light diffused by it is spectroscopically examined, the scattered radiations exhibit diminished and in some cases also enhanced frequencies. The frequency shifts fall into two classes. Some of them are very small and require, for their observation, the use of a Lummer-Gehrcke plate or a Fabry-Perot etalon; the shifts are found to depend on the direction of observation and evidently arise from the acoustic vibrations of the crystal lattice. The second group of frequency shifts may be observed with an ordinary spectroscope and correspond to those optical vibrations of the crystal lattice which are active in light-scattering. In the latter case, no variations with the direction of observation have been reported, though no very careful investigations appear to have been made on this question.

It is recognized that the scattering of light with change of frequency is a quantum effect, though it has a classical analogue which fails to represent the observed facts in essential particulars. There is thus a clear analogy between the modified scattering of light and the quantum reflection of X-rays, both phenomena arising from the inelastic collisions of photons with crystals. The wave-

length of the incident radiation is widely different in the two cases, and this is largely responsible for the difference in the character of the resulting effects. Despite the obvious differences, the fundamental similarity in the processes involved and the phenomena observed should be useful as a guide to research in both fields of investigation. In particular, it is desirable to emphasize that, as in the case of X-rays, the change of frequency observed in light-scattering should be regarded as the co-operative effort of extended domains in the crystal and not the effect of the individual ions or molecules in it.

In the literature of light-scattering, we are familiar with the idea that certain optical modes are active while others are inactive, the distinction being largely determined by the symmetry characters of the vibration. In the X-ray problem, the question whether an optical vibration is 'active' in giving a modified reflection depends on whether it modifies the structure amplitude of the particular crystal spacing under study. It is evident, however, that in the X-ray problem we are dealing with the superposed effect of all the characteristic optical modes, and cannot isolate the effect of any one of them in particular. On the other hand, we can observe the modified reflection from numerous individual crystal planes and the geometric relation of such planes to the various optical modes of vibration of the lattice cells would naturally be different. The X-ray method is also capable of application to crystals with which optical study is difficult or impossible. Hence, a study of the phenomena of the modified X-ray reflection may be expected to lead us to a deeper understanding of the problems of crystal physics, and to supplement in important respects the results of spectroscopic studies.

7. *Influence of Temperature*

The analogy with light-scattering is particularly useful in considering how the intensity of modified X-ray reflection would be influenced by varying the temperature of the crystal. As is well known, the character of the phenomena observed in light-scattering differs widely in the two cases in which $h\nu^* \gg kT$ and $h\nu^* \ll kT$ respectively. In the first case, the thermal agitation

of the system plays an insignificant rôle, and the scattering is due to its transitions from the lowest to higher energy-levels induced by the incident radiation. Hence, the scattering is with diminished frequency only, and its intensity is independent of temperature, being much greater than that indicated by classical considerations for a vibration with energy kT . In the second case in which $h\nu^* \ll kT$, the observed effects are practically describable in terms of the classical theory: the intensity of the scattering increases in proportion to the absolute temperature and appears to an equal extent with diminished and with increased frequencies. In the intermediate cases, when $h\nu^*$ and kT are of comparable magnitudes, the scattering with diminished frequency is of greater intensity than that with increased frequency. The ratio of the two tends to approach unity as the temperature is raised, and the absolute intensities of both types of scattering also becomes larger. This is because the transition probabilities for a thermally excited state are greater than for the ground state of the system.

We may naturally expect very similar results in the case of modified X-ray reflection, except that as it is not possible to separate the reflections with diminished and increased frequencies, we are only concerned with the result of their summation. As indicated by the theory, the nature of the results would depend on the characteristic optical frequencies of the crystal. At sufficiently low temperatures, the indications of the classical theory should in every case fail completely, and the quantum reflections, instead of vanishing, should be easily observable. Further, for crystals with high characteristic frequencies, the intensity of reflection should be much greater than that indicated by the classical considerations, and its increase with rise of temperature should also be slower. On the other hand, for crystals with relatively low characteristic frequencies, the increase of intensity with temperature should be very marked. Further, since this increase indicates a larger population of thermally excited states and therefore also a diminution of the static structure amplitudes, *the increase of intensity of the modified X-ray reflections with rise of temperature would be accompanied by a falling off in the intensity of the unmodified reflections.*

It follows from the foregoing remarks that theories of the temperature effect in X-ray diffraction, based on classical considerations, cannot be expected to be in full accord with the facts either at low or at high temperatures. This is indeed evident from the published literature of the subject. In the treatments usually given, however, the classical considerations are modified by taking into account the zero-point energy of the vibrations of the crystal and assuming that these have an optical effect analogous to that of thermal agitation. The static structure amplitudes of the crystal at low temperatures are thereby brought into better accord with the observed facts. It is evident, however, that except in regard to the classical or unmodified reflections, the effects produced by the crystal on the incident radiation depend on the change in the energy-state of the crystal and not upon its initial energy. The zero-point energy is, therefore, not really relevant to the discussion of such effects.

THE WONDERS OF WATER

By

I. RAMAKRISHNA RAO

1. *Rôle of Water in Nature*

Water constitutes a considerable proportion by weight of the content of the terrestrial globe, in the state of liquid on the surface, and as vapour in the atmosphere. It plays a predominant rôle in the continual geographical changes, by helping the transport of material from one place to another, thus bringing about slow but sure alterations in the distribution of matter on the earth, through the medium of rain and river water and by the continuous impact of the waves of the ocean on the shores. Because of its inherent properties, it facilitates chemical reactions between the different kinds of materials coming into contact, and becomes responsible for the considerable alterations in the geological distribution of matter. It facilitates chemical and thermal reactions in the biological kingdom by forming about seventy per cent of the constitution of animal bodies, and more than ninety per cent of the constitution of vegetable bodies.

Next to air, water is indispensable for the sustenance of all kinds of terrestrial life. It is apparently one of the simplest of chemical compounds, being constituted of one part by weight of hydrogen to eight parts of oxygen. The latter is approximately one-fifth of the atmospheric air, and is the preserver of life on this planet. With all this simplicity in its chemical constitution, its properties are most complicated and unique.

The importance of investigations on the causes of the anomalous and unique behaviour of such an interesting substance cannot be overemphasized. In the following pages, a description will be given of the various abnormal physical and chemical properties of water, and how they facilitate the wonderful rôle of this substance in

natural phenomena. In the final part will be described the researches that have led to an explanation of these abnormalities of water.

2. *Density of Water*

In so far as the absolute value of the density is concerned, water is quite normal. But the uniqueness of this substance consists in the variations of this density with change of state and of temperature. For most of the substances in Nature, the density in the solid condition is greater than that in the liquid state. It is, however, different in the case of water, ice being considerably lighter than water, volume for volume. This abnormality of water has a great influence on marine life, particularly in the polar regions, where on account of the low temperatures, sea-water freezes. If ice were heavier than water, the large sheets of it formed on the surface would have carried down with them fish and other kinds of marine life to the bottom of the sea, thus resulting in a complete annihilation of such life in these regions. But being lighter, ice remains on the surface and allows continuation of this life below it. It does something more than this. Being less conducting than sea-water, it protects the submarine life from the severe cold of the outer atmosphere and exerts a moderating influence on the severe thermal changes of the ocean.

Another peculiar characteristic of water is the anomalous variation of density with temperature. It has the maximum density at 4°C., and with further lowering of temperature, the density diminishes, unlike other liquids whose density uniformly diminishes with rising temperature. This property of water enables it to prevent large temperature variations at the lower depths of the sea in the arctic and antarctic regions. When the temperature in the atmosphere directly above the surface of the sea falls down considerably, the upper layers cool down, become denser, and go to the lower regions. By convection thus set up, the temperature of the sea reaches 4°C. Further cooling of the surface layers will prevent any continuation of these convection currents, because, below this temperature, water falls down in density again, and no further lowering of the colder surface layers is permitted. Thus

the only process by which the cold from the upper layers can be transmitted to the depths is by conduction, which is a much slower process. Accordingly high temperatures in the neighbourhood of 4°C . are maintained in the lower regions of the sea and the continuation of submarine life is made possible.

In the vapour condition, this substance is lighter than air, and as such, the continuous and abundant columns of water-vapour emanating from the surface of the sea, rise to the higher altitudes of the atmosphere. In these regions, coming into contact with the colder layers of the air, they become supersaturated and condense to the liquid state and fall down to the earth again in the form of rain. This process, not only facilitates a redistribution of water on the surface of the earth, but also plays a predominant rôle in bringing the coolness of the upper regions of the atmosphere to the lower, to the great comfort and existence of biological life. During this change, there is yet another important factor amenable to life on earth. The abundant but saline sea-water, unsuitable for consumption for such life, is continually converted into the more useful type of fresh water, which is so indispensable for this life.

3. *Thermal Properties of Water*

Weight for weight, water requires the largest quantity of heat for the same rise of temperature when compared to most other substances in Nature. Otherwise stated, the specific heat of water is much higher than that of many other substances. It is this property of water that prevents unbearable fluctuations of temperature on the earth. If water on this globe were not as abundant as it actually is, the earth would have been too hot during the day and too cold during the night, with similar extremes of weather during summer and winter. The enormous amounts of heat radiation from the sun are absorbed by the waters of the sea, without much rise of temperature, on account of the large specific heat of water, and tolerable thermal conditions are thus maintained. Constituting the major portion of the animal and vegetable kinds of life, water absorbs outside radiation and prevents any variation of their temperature.

This constancy of temperature of living forms is further facilitated by evaporation from their bodies. Water requires a great supply of heat for vaporization when compared to most other liquids. When the temperature of the atmosphere surrounding human and animal life is higher, there is great evaporation of water from these bodies, the heat required for this process being supplied by the bodies themselves. Then there is a cooling produced in them. Similarly at times when the surrounding temperature is less, this process is slower, and the heat produced in the system by internal activity is conserved. The temperature of the body is maintained at the normal level.

If the heat of vaporization of water is abnormally high when compared to that of other liquids, the cooling necessary to freeze it to ice is similarly large. Thus if some other liquid were to be substituted for water on this planet, not only would it have cooled much quicker, but would have frozen also much easier. More fluctuations in the ground temperatures, and quicker changes of state from solid to liquid and vice versa will be the result. These variations are prevented because water, with its abnormal capacity for heat, constitutes the primary liquid of the earth and not any other.

4. *Chemical Properties of Water*

It is well known that many of the chemical reactions, ceaselessly taking place in Nature, owe their origin to the presence of water. Extensive investigations in the laboratory have demonstrated, beyond doubt, how indispensable water is for facilitating these processes. The assimilation of food and its distribution in other forms to the various parts of the animal system is due to water. Plants take their supply of matter from the earth through the medium of water. This is made possible on account of the abnormal solvent properties of this liquid. In the form of solution, different substances are brought into more intimate contact for reacting with one another, which reaction would not have been otherwise possible unless very high temperatures were prevailing to enable these substances to reach the molten state for mixing up thoroughly

to react with one another. Thus water is a very convenient substitute for high temperature, without the evil effects thereof, for facilitating these chemical reactions.

The above are only a few of the wonderful properties of water. The following questions now arise. Why is it that this liquid is so stable as to form permanently a major portion of the earth's constitution? How is it that its density has peculiar variations when compared to other liquids? Why should ice be lighter than water? How is the large capacity for heat of water explained? Why should water require a larger amount of heat for vaporization, and greater cooling for freezing to the solid state than other liquids? Is there any peculiarity about water to render it so efficient a solvent? Why should this facilitate chemical reactions better than other liquids?

5. *Constitution of Water*

According to chemical investigations, water is a compound of hydrogen and oxygen. The popular conception of a water molecule visualizes it as constituted of two atoms of hydrogen and one of oxygen. It is symbolically represented as H_2O , but the water molecule is not as simple as that. That the constitution of the water molecule is complex was postulated long ago. But this postulate had no direct confirmation from experiment. It remained, till very recently, a hypothesis, propounded to explain the anomalous behaviour of water.

The ocular demonstration of the complex nature of the water molecule has been made possible by the author and his students by a study of the Raman spectrum of this substance in its different phases. If water is anomalous in its physical and chemical properties, it is much more so in its Raman spectrum. While most of the substances, so far studied, give rise to sharp and narrow Raman lines, water exhibits a very broad and diffuse band. The uniqueness of this phenomenon with water does not stop here. While with most other substances, the changes in these lines with change of state (e.g. from solid to liquid or liquid to gas) or of temperature, are inconspicuous, with water they are otherwise. The diffuse and

broad Raman band of this substance resolves itself into two narrow portions for ice, and to a single sharp line for vapour. At higher temperatures, this band shifts towards the line corresponding to the vapour, and lowering of temperature makes it similar to that for ice. Similar changes in the position and structure of this band take place when foreign substances are dissolved in it, the effect being similar to that due to increase of temperature.

This peculiarity in the behaviour of water in respect of its Raman spectrum has been explained on the basis of the anomalous constitution of the water molecule. This molecule is not of the simple type, usually represented symbolically as H_2O , but is more complicated, being in aggregates of two's and three's, and capable of representation as $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ to be hereafter called the *water* and *ice* molecules respectively, which act as units, present in a state of equilibrium with single H_2O 's (to be hereafter called the *vapour* molecules). It is the change in the equilibrium between these three kinds of molecules with change of state or of temperature that is responsible for the uniqueness in the behaviour of water.

If water were to consist of vapour molecules only, it would have existed as a gas at the temperatures prevailing on the surface of the earth. It is the possibility of association of these groups, which are more stable in the liquid condition, that raises its boiling point by about 200°C . above what is required by the simple constitution, thus enabling this substance to remain as a stable liquid. This process of association in water is thus what makes the earth what it is with its animal and vegetable life and its distribution of land and sea.

In the liquid state, all the three types of molecules postulated above are present, their relative proportions changing with change of temperature. In ice, there are only *ice* and *water* molecules, the former being in greater abundance. It is these two types that are responsible for the doublet structure of the Raman band of ice. In the vapour state there are only single molecules, which give rise to only one line in its Raman spectrum. In water at low temperatures, the *ice* molecules are in greater proportion than the *vapour* molecules, and with increase of temperature, the former diminish in

numbers changing over to the *vapour* type. *Water* molecules are most stable in the liquid, and are most compact in packing. The stability of *ice* molecules is less, and their density of packing loose.

The above picture of the constitution of water enables us to explain the various abnormal properties of this substance. On account of the greater preponderance of the *ice* molecules in the solid state with their loose packing, ice is lighter than water. In the liquid state, the proportion of *water* molecules is greatest at 4°C. The fact that their packing is closest, is responsible for the maximum density of water at this temperature. Above or below this, the proportion of the other types increases naturally resulting in a lowering of density.

The explanation of the thermal rôle of water on the basis of the association hypothesis is still more wonderful. With most liquids, the heat supplied is utilized to separate the constituent molecules to greater distances, thus raising their temperature. But with water, this heat has to do two kinds of work. Not only is the heat supplied utilized in separating the molecules, but it is to a large extent used in splitting up the more complex *ice* and *water* molecules into the *vapour* type. This latter process does not involve any rise of temperature. Thus for water, more heat is required to raise it through a certain range of temperature than for other liquids. In other words, the highly associated state of water is responsible for its large capacity for heat, and this is the primary cause of the moderating influence of this liquid on, what would have otherwise been, colossal variations of temperature.

If water requires a large amount of heat for change of temperature, much more is this energy required for change of state. With other substances, the molecular arrangement is altered at the expense of the heat supplied during the process of change from the solid to liquid, or from the liquid to the gaseous phase, without change of temperature. In the case of water, the heat required for change of state is not only to alter the molecular arrangement, but also to convert the associated molecules to lower polymers. That is why this liquid consumes a larger amount of heat during vaporization and melting than other substances.

Water has a large dielectric constant. This property enables this liquid to minimize the electrical forces between molecules of substances dissolved in it to a much greater extent than in other liquids. This is what makes water so efficient a solvent. On account of this property, it has a very high ionizing power. When most of the inorganic substances in Nature are dissolved in it, their molecules are split up into the respective positive and negative atoms or groups of atoms that constitute them. In this state, these electrically charged atoms or groups are much more active chemically. Hence when substances in aqueous solutions are brought into contact, they chemically combine more easily. It is in this manner that water functions as an agent for chemical reactions, and the high dielectric capacity for water, which is responsible for this, is due to its associating power.

Thus the high association in water, on account of which more complex molecules are formed in it, is the cause of the unique rôle of this substance. It is this that makes it so stable and so abundant a liquid. It is again its association that renders water so peculiar in its density characteristics. The large capacity for heat and high latent heats of fusion and evaporation are consequences of this association.

THE PLANNING OF SCIENTIFIC AND TECHNICAL RESEARCH IN INDIA

By

H. K. SEN

The existing research establishments can be broadly divided into those under the universities, those under the Central and Provincial Governments, and those under private enterprises. The last include research laboratories of industrial concerns and private laboratories where work is carried on with a view to establish some industries for which the country offers possibilities. Whatever may be the categories under which these research establishments can be brought, the most important consideration would be the reorientation of research problems with reference to national needs. Whilst co-ordination of researches undertaken in the various laboratories would be a most essential condition, a scheme for investigating specific problems necessary for the development of key industries in the country would be of far greater importance. It must be acknowledged that at the present moment, there is a good deal of confusion in the choice of problems in research laboratories, both chemical, physical, engineering and applied. This confusion may be said to have arisen mainly on account of the absence of a clear objective for research, for, in the universities, researches, whether pure or applied, are looked upon only as pieces of intellectual exercise, and in other establishments not a little of the handicap is due to having to cut their coat according to the cloth. There are honourable exceptions, but in the main, it is true that research workers in India, having till lately neither clear-cut objectives nor adequate equipments, have attained only a moderate amount of success, and their efforts have practically led to little industrial development. Too much energy and considerable funds are inappropriately used in the universities—as yet real centres of research—in not concentrating on specific and useful problems.

There is a tendency to drift from one to the other as something must be produced to meet the degree requirements of universities, and often materials are wasted to bring about fanciful results under the garb of theoretical researches. I must emphasize, however, this is more with regard to theoretical researches, where the latitude of the worker is limited only by the resources of the laboratories where he works. Inadequacy of equipments, born not so much out of absence of funds in some cases as of extravagant use of chemicals and careless handling of apparatus, could be considerably remedied, if more thought were bestowed on the annual purchases of each laboratory. Further, the difficulty in obtaining normal supplies of chemicals from abroad makes it incumbent upon us both to economize and to prepare them in this country. I cannot help sounding a note of warning, not only in view of the present crisis but as a rule of general practice, that the habit of working with very much smaller quantities of materials should be strictly enjoined upon students and research workers. In these days of microanalysis, microtests, and microvessels, the classical tendency to start with 5 or 10 grams of reacting materials has generally no significance. I once calculated that only by economizing in this direction, a laboratory made a saving of Rs.3,000 in one year out of a total grant of Rs.15,000 for chemicals and apparatus. Such habitual economies will obviously give more funds for the purchase of useful equipment which are so wanting in most laboratories in varieties and number.

Co-ordination and Guidance

A question of very fundamental importance in evolving a practical national scientific planning is, How are these laboratories to be equipped and co-ordinated in order to get the best results? The idea of co-ordination has much to recommend itself in view of the economy that is possible to secure, and individual and collective initiative may be fully secured by allotting specific responsibility. There is thus clearly a need for educating research workers to be able to work in a team and I do not know of any method of securing complete co-operation between the different links of a

co-ordinated research except by proper recognition, individually and collectively, of all the workers in the whole scheme. My experience of a third of a century, both as a young worker under tutelage and as a collaborator at a later stage, has confirmed the impression that there is not adequate recognition for junior workers in a co-ordinated scheme. The senior, whenever he has been able to give unstinted recognition to his juniors, has invariably been able to produce the best results out of a piece of research. I consider, therefore, the guidance of research is far more important at this stage than research itself. The guide must be in a position to create conditions under which successful researches can be carried out, and it would be no small credit for him if the individual workers under him complete successful investigations.

Equipment

Whilst a few of the laboratories have sufficient finances to enable them to equip themselves for general research purposes, many industrial processes, requiring extreme conditions of pressure and temperature, call for specially costly equipment which might not be within the means of any individual research establishment to acquire. As far as possible, attempts should be made to develop certain central laboratories so as to tackle problems of such specialized nature, and render available the occasional use of such specialized apparatus to other laboratories where there are none. I do not know exactly what is or will be the position of the National Planning Committee, and how far its recommendations will be binding on or acceptable to existing laboratories, but it certainly could invite heads of all laboratories for a special conference on this question, and secure voluntary co-operation on the lines indicated. It will still be necessary for the Planning Committee to face the necessity of having special research laboratories for the investigation of the more important raw materials of the country and a power and plant design laboratory to aid in the establishment of industries. The Government has already taken steps in the matter by the establishment of special laboratories for investigating cotton, jute, sugar, lac, and tea. To my mind, a

specialized fuel and power laboratory, and an engineering laboratory with the object of plant designing would effectively meet the situation for the present. The scope of the latter would doubtless have to be increased by making pilot plant trials possible under its auspices. The manufacture of heavy and fine chemicals is a growing necessity, and, as indicated before, for this, the basic or key chemical industries must be ushered into existence where there are none. The research background for both, particularly for the latter, is very extensive, and the most economical way to meet this requirement best would be by distributing specific problems to the research establishments, university or otherwise, throughout the country. In fact, most laboratories are in a position to contribute to the solution of this part of the problem as the equipment, except in special cases, are within the reach of almost every well-organized laboratory. I would insist that all research laboratories should have each an efficient workshop, not to speak of glass blowers, to help in the construction of research apparatus. This probably would be the quickest way of beginning to tackle problems catalogued by the National Planning Committee.

To co-ordinate all such or specially established research laboratories, a representative committee will have to be set up, something like a National Research Council, whose business it would be to direct the attention of research establishments to problems of research to further the objectives of National Planning.

Synthetic Fertilizers

Whilst it is not my object to discuss fully the key industries, a few outstanding problems may be indicated. The agricultural industry is undoubtedly the most important one requiring immediate attention. With a population of 400 millions which is on the increase, the food grain produced in the country can hardly be supposed to be sufficient for its proper nutrition. Then food, though the most important, is not the only essential requirement of a man. He has to part with a portion of his agricultural produce for purchasing other accessory requirements like clothing, housing, transport, medicine, etc. This reduces his food availability still further and the natural

conclusion is that the land must be made to yield more than it is doing to-day.

The development of an artificial fertilizer industry is admittedly the quickest way for coping with the situation, leaving aside for the present the question of bringing in further areas of land under cultivation. In order that such fertilizers can be within the reach of the cultivator, their prices must be very low, indeed very much lower than prices at which fertilizers are now imported. To start with, one should examine the existing fertilizer requirements of the country. It is true, at the present moment, artificial fertilizers are being mainly, if not entirely, consumed by tea estates and sugar plantations. The use of artificial fertilizers in the latter is as yet very restricted, and in the production of food crops like rice, wheat, lentils, etc., there is hardly any. The present import figure of ammonium sulphate is about 76,000 tons per year. But with a scheme of general manuring dependent upon artificial fertilizers, its quantity would have to be multiplied by 10, if not by 20 in the nearest future. The manufacture of ammonium sulphate, therefore, offers an excellent field for research. There are at present two well-defined processes for the manufacture of ammonia, one as a by-product of coal distillation and the second, by the catalytic combination of nitrogen and hydrogen. The by-product recovery again can be classified under three distinct heads: (i) from the high temperature distillation of coal for the gas and the coke industry, (ii) from the low temperature distillation of coal, and (iii) by Mond gasification or a combination of low temperature carbonization and subsequent Mond gasification of the soft coke. As the Mond gasification is mainly associated with furnace firing, steam raising, and power production, the scope of this process is dependent on the magnitude of such undertakings. By the Mond process, about four times more ammonia than by high temperature coking and eight to ten times more than by the low temperature carbonization are available. The by-product manufacture of ammonium sulphate is well understood in the country, and already some quantities of it are made, but since its manufacture depends upon the distillation of coal, to that extent its quantity is restricted, and unless more

extended coal distillation could be envisaged, a national fertilizer industry dependent upon by-product ammonium sulphate alone is not possible. Even then, the question of supplying the requisite sulphuric acid to the ammonia equivalent has to be critically examined, for, we have as yet no reliable source of sulphur in the country. The practicability of using gypsum in this connection should be thoroughly gone into, both as regards its availability and cheap transport to coal areas. If this is found to be a suitable source of extracting the sulphate ion for the fixation of ammonia, the catalytic combination of nitrogen and hydrogen gives an unlimited possibility. I do not propose to go into the details of the syntheses of ammonia which are well known, but what I do want to emphasize is the vast amount of research that is necessary to supply the background of this industry in the country. It may be contended that this problem is so well worked out in foreign countries that through the assistance of foreign experts and foreign plants, the establishment of this industry is possible. I admit this possibility, to begin with, but ultimately the plants should be made in India and worked by Indian personnel if the price is to be kept within the reach of the poor cultivators. The prevailing price of imported ammonium sulphate is of the order Rs.100 per ton (pre-war price) and to induce the cultivator to use it, it will have to be no more than half, if not a third, of this price. Even when imported expert labour and plants are replaced, the need for the encouragement of systematic research, both chemical and mechanical, to cope with future eventualities, cannot be too highly emphasized. The fertilizer industry is so important that the creation of a research nucleus to further this object is long overdue. As far as I am aware, the resources and equipment available at Bangalore, Calcutta, Lahore, Allahabad, and Waltair, if co-ordinated, could cope with all aspects of this important investigation.

It may be appropriate at this stage to dwell somewhat at length on the technical aspect of a nitrogen fixation industry in this country, in order to throw light on the specific nature of researches that must be developed to build up this huge and complicated industry for the agricultural prosperity of the country.

Looking through the extensive literature on the subject of nitrogen fixation, one is amazed at the persistent and continued efforts to discover newer methods, in spite of the two well-known processes that are commercially practised to-day. The complicated technique of both renders their adaptation no easy task, where the plant construction alone requires exceptional skill and knowledge of the quality of materials. The high pressure under which the Haber process is carried out is in itself a sufficiently discouraging feature to start with. A sound mechanical and metallurgical industry must be the background for such constructional feats. Many accidents, much sinking of funds and continued application of human ingenuity made the Haber process a successful commercial proposition. The amount of constructional researches for developing the right plant for the carrying out of the process is simply bewildering. To establish this industry on a national basis, we would have to pass through many, if not all, of the stages that led to its unique development. If this is on the mechanical side, the chemical side is no less difficult. Researches on the most suitable catalyst as to reactivity and life, the manufacture of the two gases nitrogen and hydrogen in a requisite state of purity, the control of temperature, the space-velocity for optimum yield, etc., have busied hundreds of workers for a quarter of a century before the process reached its present perfection, and even then there is no cessation of research to improve and simplify further. The conclusions are obvious. But all that trouble is worth while taking when one remembers that as a result of the Haber process, two bushels of corn can be grown where there was only one before. Not that here in India we could not adapt the process, but the difficulties associated with its introduction are many. Here lies the need for the foresight of our legislators, the imagination of our chemists and engineers, and the most perfect co-ordination, that I am pleading for.

It might be asked whether the introduction of such a synthetic fixation of nitrogen is an immediate problem, when about 3 million tons of coal are already coked. The 3 million tons represent under coking condition barely 30,000 tons of ammonium sulphate. As far as my information goes, about half of this ammonia is actually

recovered, but if all were recovered, there would still be the need for 46,000 tons of ammonium sulphate at the present import figure. As a matter of fact, the soft coke industry, which uses a little over a million tons of coal per year, could easily supply the extra need if rationally conducted. Ordinarily a ton of coal carbonized between 500–600°C. would give only 10 to 12 lb. of ammonium sulphate as by-product, but the hydrogen of the gas could be used for fixation of nitrogen under suitable conditions. Thus, the 1.2 million tons of coal would yield approximately 6,000 million c.ft. of gas, of which about 1,000 million c.ft. is hydrogen. This hydrogen, when converted into ammonia with atmospheric nitrogen, would yield 22,000 tons of ammonia equivalent to 88,000 tons of ammonium sulphate. To this, if ammonia recovery as by-product be added, a total production of 95,000 tons of ammonium sulphate can be envisaged. By increasing the dimensions of either type of carbonization, no doubt the output of by-product ammonium sulphate could be increased, provided the excess of coke and soft coke could be disposed of.

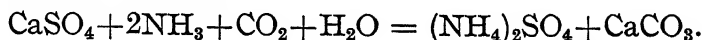
On the other hand, the fixation process is a self-contained one, in which there are no by-products to be disposed of. It could also be made an adjunct to any of the coking establishments. By the liquefaction coal gas and atmospheric air, both hydrogen and nitrogen, necessary for the catalytic process, could be manufactured in unlimited quantities, and, in fact, the gas, which is often a drag on the coking industry, could thus be successfully utilized. It is well known that the gas produced by high temperature coking or by low temperature carbonization is rich in methane. The problem of cracking it to enrich the final gas with hydrogen is obviously an important one in the nitrogen fixation industry.

An approximate calculation of the cost of producing ammonia by fixation may not be out of place here, as it will open our eyes to the drainage of vast sums of money that is annually taking place by the importation of ammonium sulphate, and the low cost at which it could be manufactured in the coal areas as shown below, based on English figures.

Cost price of one ton anhydrous ammonia from a 60-ton daily unit

						£	s.	d.
Depreciation, interest, machinery	$\frac{406,286 \times 0.16}{350 \times 60}$	3	1	10
.. .. buildings	$\frac{30,951 \times 0.11}{350 \times 60}$	0	3	3
Coal 1,900 kg. at 5s. 11d.	0	11	2
Workmen 6.5 h. at 6d.	0	3	3
Water 250 cm.	0	1	1
Copper 0.14 kg. at 11d.	0	0	2
Formic acid 0.84 kg. at 1s. 4d.	0	1	2
Electric energy 1,600 kwh.	1	0	0
Maintenance and sundries	1	2	6
TOTAL						6	4	5

A question of very fundamental importance is raised in this issue of the home-manufacture of ammonium sulphate. Even concentrating on the production of 76,000 tons of it (the present annual import figure), we would have to find about 57,000 tons of sulphuric acid or 19,000 tons of sulphur, every ounce of which is imported to-day. In my Annual Address before the Bihar Branch of the Institution of Chemists (India), I had suggested last April the use of gypsum in the manufacture of ammonium sulphate. A thorough survey of the economics of the supply of this mineral to the coal areas and some preliminary experiments on the manufacturing conditions of ammonium sulphate according to the following reaction are necessary:



An alternative process for the manufacture of sulphuric acid from gypsum is also well known, but in all such operations the preliminary trial with pilot plants would save many thousands of rupees. These would involve researches in technical chemistry and industrial engineering, for which, by co-ordination, satisfactory arrangements could be made. It may be indicated that even a syndicate to test such and other problems on the basis of private interests may satisfy the present situation.

A problem no less fascinating and important is the manufacture of commercial urea, where the sulphuric ion is altogether obviated by carbon dioxide. The suitability of this material for manurial

purposes has not been definitely established in this country, but as a problem of agricultural importance, and chemical self-sufficiency, the most earnest examination of this matter by chemists, chemical engineers, and agriculturists is urged. My own experiments on a semi-pilot plant scale have convinced me about the economic feasibility of the conversion of ammonia and carbon dioxide into urea, and apart from its use as fertilizer, its importance in the synthetic resin industry is too well known. The cost of manufacturing urea may be easily put down at Rs.110 per ton from synthetic ammonia, and one ton of urea is equivalent to $\frac{46.6}{21.22}$ or 2.2 tons of ammonium sulphate. In other words, the nitrogen equivalent of one ton of ammonium sulphate can be had for Rs.50.

Power Production

For a scheme of national industrial development, on a par with other countries and in keeping with the modern tendencies of locomotion, nothing is so important as the foundation of a cheap and sound supply of power. It is a basic problem for the solution of which all the sciences have to co-operate, and one in which even the housewife is interested. With the progress of civilization, the primitive methods of firing, followed till lately, have given place to that vast industry called the fuel industry which is now a subject of the most complicated research in chemistry, physics, geology, and engineering. From the burning of wood in forests for producing charcoal to the distillation of coal and peat, the human race has travelled a long way, in which chemical research has played a most important part. Doubtless, the ever-increasing dread of the shortage of fuel has led the chemist, as also the engineer, to treat these raw materials in such a way as to secure the maximum efficiency of heat and motion therefrom. India is fast breaking away from its primitive rural conditions, and with its numerous furnaces, boilers, locomotives, internal combustion engines, and the many more yet to come, fuel research takes a very paramount position. This should lead to the manufacture of different types

of engines and tractors suitable for various fuels. It is to be regretted that no step has yet been taken in the country to better utilize our meagre fuel reserves. India has no more than 1% of the total coal deposits of the world and probably even less of mineral oils. This makes fuel economy far more imperative and attempts to utilize the thermal energy of the sun a problem of the highest interest. Amongst the latter I might indicate not only the direct energy of the sun but also the forest and waste agricultural resources. In all these, chemical researches combined with the mechanical would be a fruitful task. From these generalizations I come to one particular instance, the carbonization of coal for power production. The chemist has not only improved the efficiency of the utilization of this naturally occurring fuel but also, in the process of preparing it, won many products so indispensable to modern civilized life. Coal-tar distillation and the cracking of petroleum residues have given rise to many useful chemicals and solvents. Industrialized India has here a vast field for chemical and physico-chemical researches.

Engineering and Metallurgy

With considerable mineral deposits in the country, India's dependence on imported metals and alloys is very much to be deplored. That far-seeing businessman, J. N. Tata, laid the foundation for the first large-scale metallurgical works in this country 25 years ago, which is now the pride of the nation. Its resources and the new laboratories can afford facilities for metallurgical researches of various types and one can look forward to a complete development in this country, at least, as far as iron and steel are concerned. We have yet to develop suitable metallurgical centres for copper, aluminium, manganese, lead, etc. in all of which research will play an important rôle. With a proper development of our mineral resources and application of chemical and engineering skill, India could not only be independent of imported metals and machines but export them to other countries instead of, as now, exporting shiploads of our mineral deposits and importing metals, alloys, and mechanical appliances.

Acids, Alkalis, and Salts

As long as there is no self-contained sulphuric acid industry in India, she could never conceive of a rational development in chemical industries. The investigation of the few deposits of pyrites in India, and the possibility of utilizing gypsum and the meagre sulphur in most coals of the country, would form a very important field of geological as well as chemical work. Further to this, the economics of using zincblende from Burma and copper pyrites of Musabani deserve to be investigated. These works are no doubt capable of being conducted on already known lines, but their adaptation and introduction in this country are problems in advanced chemical engineering for which encouragement and organization are necessary.

The alkali industry is in a rather peculiar position in this country. Where there is salt, power is dear and vice versa. A careful striking of a balance sheet shows, however, that both the electrolytic process and the ammonia-soda process come within economic possibility in well-conducted factories. A most important consideration in this connection, as, indeed, with reference to other industries as well, is the construction of appropriate plants in India. The cost of imported plants and machineries together with occasional replacements is often so high that the establishment of a competitive basic industry is well-nigh impossible. In the establishment of a heavy chemical industry, therefore, whilst many of the processes are well understood, their introduction in the country suffers from this handicap, but they are of a nature which by trial and error could be overcome. This is a field where the chemist and the engineer have to work hand in hand to create a proper condition by pilot-plant trials for the manufacture of such plants. The present cry for the establishment of a chemical industry would be in the wilderness and, indeed, expose the height of ignorance if any attempt to manufacture chemicals, inorganic or organic, be made without a sound acid and alkali industry backed by a national machine industry. To reproduce known processes on a commercial scale is a research by itself.

Having most of the ores and minerals in this country, the establishment of an acid industry would automatically lead to the manufacture of all the necessary salts.

Fibre Industries

Whilst the textile industry, as based upon cotton, is fairly well established in India, and the Government has made it possible to ensure further developments by the establishment of the cotton laboratories in Bombay, the production of artificial silk is as yet a subject for research, although it could follow only in the wake of chemical industries. In the meantime, however, there is need for the systematic investigation of the available resources of the country as to their suitability for the production of artificial silk. One cannot help making a passing reference to milk-silk in this country.

With 45 to 50 thousand tons of paper and pulp annually imported into the country, the task before us is clear. The chemicals required in their manufacture are greatly, if not entirely, imported, and an investigation on the production of similar materials would ultimately pay.

It is most gratifying that the monopoly fibre of India, jute, is being investigated for the first time in the country of its origin systematically and thoroughly. I well hope that this fibre, which is the largest cash crop of India, will play a more important part than it has in the past and I note with a degree of satisfaction that one university at least, under the able guidance of Dr. J. K. Chowdhury, has conducted important work on the chemical and practical sides of the jute fibre. The newly instituted jute laboratory in Calcutta has a great rôle to play in converting this raw material into a variety of articles of everyday use.

Industrial Solvents

Solvents are the hand-maiden of organic chemical industries and by far the most important of these are obtained by coal-tar distillation, fermentation of saccharinous materials, hydrolysis of pentosans, and catalytic hydrogenation of carbon monoxide. These are the pre-requisites for the manufacture of synthetic drugs,

fine chemicals, pharmaceuticals, etc. The solvent industry, therefore, can be considered as a basic one, and so varied are the details of their manufacture that a sound research background is necessary for its initiation and development. The increasing use of furfuraldehyde in petroleum refineries, paints and varnishes makes it an important solvent for the manufacture of which raw materials exist in the country. Then there are the derivatives of ethyl and methyl alcohols which are indispensable in the arts and industries. The catalytic oxidation of these into aldehydes and acids, the fermentation of the starches into butyl alcohol and acetone, the production of butane from cracked petroleum are some of the instances which call for intensive chemical research.

Organization of Industrial Research

In the application of chemistry to industry, the engineering aspect is as important as, if not more so than, chemical knowledge, and applied chemical research which is the foundation upon which to build chemical industries is, with rare exceptions, woefully lacking in this country. We have capable chemists and engineers but not chemical engineers. The trend of teaching chemistry in this country has been to emphasize theoretical knowledge and practical technique only up to the laboratory stage and no further. The time has now come when the problems of the application of scientific principles to the economies of life must be seriously tackled. This can be attained by the establishment of specially equipped chemical engineering research laboratories with facilities for pilot-plant tests in which the industrialist, the engineer, and the chemist should co-operate wholeheartedly. The most important development necessary at this stage is the training in industrial technique in general, viz. large-scale evaporation, distillation, high pressure experiments, low temperature work, handling vacuum apparatus, modern refrigeration practice, preparation of industrial catalysts (chemical and biochemical), absorbent materials like alumina, silica gel, active charcoal, etc. Before the chemist who knows all about the manufacture of ammonium sulphate in the laboratory can put tons of it on the market, he must go through the above-mentioned course of

industrial technique. Apart from the physical or engineering aspects of the high pressure technique to bring about chemical processes, it has often to be aided by catalysts, a very intensive study of the science and practice of which is necessary. Enough attention to my mind has not been paid to this important and ever growing subject, whether from the theoretical or from the industrial point of view. Taking a very wide view of this subject, biochemical catalysis is probably of far greater importance in human economies than many of the induced catalyses of inorganic chemistry. The easy availability of micro-organisms, their specificities, the wide ranges of choice, and possible acclimatization, all these make them tools of far greater utility than the usual catalysts in carrying out delicate processes. Even they do not lack in speed, when we think how a few ounces of yeast can convert tons of sugar into alcohol overnight almost without our having to look at it! Then the enzymes which form, as it were, a link between the living and the non-living, are still less explored in this country, whilst their uses in many medicinal preparations are not inconsiderable. There are isolated instances where work in this direction is in evidence, but a centralized laboratory for the investigation of catalysts and colloids appears to me of the utmost importance in furthering our industries. I will cite an interesting instance of which I have some experience: A single passage of a requisite mixture of hydrogen and carbon monoxide or dioxide, over a microbial bed prepared from sewage, is capable of converting it into methane. The process is still in its infancy, but think of its potentiality in converting the cheap but highly poisonous water gas into innocuous methane for general utilization. Many of the problems of waste products utilization would be commercially feasible if our attention is directed to this aspect of chemical research. Whilst I have urged for an intensive research background in applied chemistry, I cannot help laying emphasis again on the practice of initiating pilot-plant-scale trials which is the half-way house between chemical research and industries. This practice is well recognized in all industrial countries before a particular industrial process is launched on a large scale. I may be pardoned if I alluded to its fruitful nature in relation

to an industry with which I am concerned, viz. lac. The Indian Lac Cess Committee has shown proper sagacity by affording unstinted support in working out a process for the industrial manufacture of shellac plastic materials through the stages of laboratory research, pilot plant, and co-operation with industrialists, the results of which are already being felt in the manufacture of electro-technical goods.

I should refer in this rapid survey of the task ahead of national scientific planning to the need for the establishment of a central library and information bureau which should actively supply all the required technical literature and patent specifications to those interested. We have already the nucleus of such an organization in the Industrial Research Bureau of the Central Government, but its scope requires considerable expansion.

I cannot conclude this rapid survey without referring to the financial aspect of the proposed developments. Whilst the State has its responsibilities and which fortunately it has fulfilled to a great extent by the establishment of research institutions, the co-operative contribution of the existing industries could meet the necessary wherewithal for the establishment of central technical laboratories equipped for all types of large-scale industrial trials. A lesson in this direction might be gleaned from the scheme of work of the Kaiser-Wilhelm Gesellschaft for the development of scientific research in Germany.

H.E. SIR ARTHUR HOPE AND DR. C. R.
REDDY AT THE LATTER'S ŚAṢṬYABDAPŪRTI
CELEBRATIONS OVER WHICH HIS EXCEL-
LENCY PRESIDED.

VICE CHANCELLOR



THE WAR AND ITS REPERCUSSIONS ON THE CHEMICAL INDUSTRIES OF INDIA

By

J. C. GHOSH

The modern war is fought on a totalitarian basis. It is hardly confined to the scene of engagement between the armed combatants. The industrial worker is now as much a part of the war machine as the actual soldier, and every effort is therefore now made to paralyze the industrial activity of the enemy nation. With her unchallenged supremacy at sea, England has blockaded Germany and cut off all her maritime trade. This blockade was not absolute for the first eight months of the war, for there is no doubt that neutral countries like Italy, Switzerland, Belgium, Holland, Norway, and Sweden acted as clearing houses for considerable export and import of goods to and from Germany. But the situation changed completely in the fateful months of April, May, and June, 1940, and now practically the whole of Europe, except the United Kingdom, has been cut off from Indian trade. The loss of export trade to the Continent of Europe has entailed great hardships on the Indian growers of groundnut, coffee, and jute. Frantic efforts are now being made to discover new uses for these materials. For example, industrial research has just been undertaken by Dr. Bhatnagar at Calcutta with the object of manufacturing synthetic plastics out of coffee beans. The exportable surplus of groundnut crop is about 7 million tons annually. The possible use of groundnut oil as substitute for mineral lubricating oils, which we import every year to the extent of 40 million gallons, is under investigation. The chief problem is to find out suitable antioxidants which will prevent gum formation and change in viscosity due to contact of oil with air and heated metal parts.

While the prices of these raw materials are tumbling down, those of commodities which were largely imported from Continental

Europe are soaring high. The rate of rise in the price is partly a measure of our dependence on enemy countries for their supply and partly a measure of the consumption of these goods in the manufacture of munitions. For example, the rise of 50% in the price of aluminium is due more to the unlimited quantity of this material needed for the manufacture of aeroplanes rather than to the blockade of enemy countries. In India, advantage has been taken of this situation by the Canadian Aluminium Corporation which are putting up a factory for the manufacture of aluminium in Travancore. The hydroelectric power available in the State will be supplied to this company at a special concession rate. It is hoped that the valuable deposits of bauxite in the Ratnagiri districts will be ultimately used for the manufacture of pure alumina. An Indian company was floated some time before the war to manufacture aluminium at Asansol; it was estimated that electricity could be generated by coal at pit's head at a cost comparable to that of hydroelectric power. Owing to the war, the power plant for which orders were placed with the Skoda Works at Czechoslovakia could not unfortunately arrive in India, and the company is now in a state of suspended animation.

A bird's-eye view of the import figures of heavy chemicals in India is instructive. The total value of imports, excluding fertilizers, amounted to 3·3 crores of rupees in 1937-38, Great Britain supplying about 54% of our needs, and Continental Europe only about 25%. Soda ash, caustic soda, and other soda compounds to the total value of 1·2 crores of rupees were mostly supplied by the Imperial Chemical Industries Ltd. This gigantic monopoly has not fortunately taken advantage of the war to make excess profits; and their old customers in India are receiving their normal quota of these goods at reasonable prices. The new customers are in a difficult position, no doubt. But we hope their difficulties will soon be removed. A factory is being put up in the neighbourhood of Calcutta by the Imperial Chemical Industries (India) Ltd. for manufacturing soda ash, caustic soda, chlorine, and bleaching powder. Under the aegis of the Tata Chemicals Ltd., a similar factory is in the course of construction in Western India at Okha port where

common salt can be had in abundance. Here again the difficulty has been one of importing suitable machinery. All on a sudden, the Scandinavian countries, which manufacture excellent electrical machinery, found themselves involved in the war; and orders for machinery placed with these countries had to be transferred elsewhere with the result that progress in construction has been considerably delayed. Both the enterprises have, however, huge capital resources at their back; and we hope that before long, these initial difficulties will be overcome, and Indian consumers of alkali and chlorine will be able to enjoy the benefits of a competitive market.

While the trade position as regards alkalis has been fairly normal, there are certain heavy chemicals which have enjoyed or are enjoying a price boom due to special reasons. For example, take the case of bleaching powder. At the beginning of the war it was anticipated that intense gas warfare would prevail, and that chlorine would be used not only for offensive purposes, but also for decontaminating areas subjected to attacks of mustard gas. The export of bleaching powder and chlorine from the United Kingdom was only permitted in special circumstances; and they became rare commodities in India. The result was that many textile mills in India put up small electrolytic chlorine plants of their own. This development in turn has brought to prominence the question of manufacturing graphite electrodes in India; and the Board of Scientific and Industrial Research is financing a research in the Indian Institute of Science regarding the graphitization of moulded carbon electrodes at the high temperature of the electric furnace. The question of the supply of chlorine and bleaching powder is not, however, an acute one at the present moment, as the Imperial Chemical Industries (India) Ltd. are reported to have started production. A plant for the production of caustic soda and chlorine was put up at Mettur about a year and a half ago at a cost of Rs.9 lakhs, with concessions from the Madras Government regarding the supply of electric power and water. For lack of fluid capital the plant has been idle so long. It is understood that Seshasayee Bros. of

Trichinopoly have now taken up the management, and that under their supervision the factory will start work immediately.

Sodium and potassium dichromate furnish another example of soaring prices due to war needs. This material is largely used in the mineral dyeing of cloth in Khaki which is the standard colour for the uniform of the British Army. The price which was Rs.30 per cwt. before the war rose even to Rs.180 per cwt. some time ago and now stands at Rs.60 per cwt. Mysore produces the finest chrome ironstone in India and has built up a flourishing export trade with America. Our normal peace-time requirements are 2,000 tons approximately. As a result of investigations in the Indian Institute of Science, a new type of stationary furnace with electrical heaters has been devised which will use, for the process of roasting the ore, the pure oxygen available as a by-product in the synthetic ammonia factory at Belgula. It is hoped that by a judicious blending of the ore, lime, and soda and the use of pure oxygen, the conversion of the ore into chromate may be effected at a lower temperature. The factory which is being put up by the Mysore Government under the supervision of Dr. K. R. Krishnaswami is expected to start production shortly. Attempts are being made in many parts of India to utilize vegetable dyes for Khaki cloth, and researches are in progress under the auspices of the Board of Scientific and Industrial Research to produce by this process Khaki cloth having the requisite fastness of colour. In the Bombay University Laboratory, a process has already been evolved in which cutch is used as the raw material; and large-scale tests of this process are now being conducted by the Bombay Mill Owners' Association at the instance of the Supply Board of the Government of India.

The Indian match industry presents a peculiar problem. Thanks to the protectionist policy of the Government of India, Indian factories now produce all the matches that are consumed in the country. As a matter of fact, the Central Government derives a handsome revenue by the imposition of an excise duty on this industry. Potassium chlorate, one of the main ingredients in the match heads, is considered an explosive, and its transport by sea in these abnormal times is not encouraged. The price has accordingly

gone up several hundred per cent, and the indigenous manufacture of this article has become an urgent war problem. This should not be at all difficult to achieve in India where an adequate supply of chlorine will be forthcoming at an early date.

In the case of many heavy chemicals on the other hand, the price has gone up not only because of an abnormal increase in demand but also because they were mostly imported from enemy countries. Sulphur is one of such key chemicals. About 36,000 tons were imported in 1937-38, Italy supplying 65% of our requirements. The present price is Rs.200 a ton as against the pre-war price of Rs.80. As a result, sulphuric acid which forms the basis of all chemical industries now sells at Rs.160 a ton. Attempts are being made to discover sources of sulphur within the country itself. It is estimated that in the works of the Indian Copper Corporation about 6,000 tons of sulphur escape in the air during the roasting of the chalcopyrites. Processes have now been perfected, specially in Canada, to recover this sulphur, and it is worth while considering if a similar process cannot be used with success in India. Deposits of pyrites have been reported from several places in India, e.g. from the Shahabad district in Bihar and from the Simla Hills. The latter deposit has been carefully surveyed and appears to be both valuable and extensive. It is hoped that special concession in railway freights will make this source of sulphur available to the industrialists of India. The Geological Survey of India have also begun prospecting work for sulphur in the Baluchistan area, and the results of their preliminary investigations appear to be promising.

The German and French Potash Syndicate operating the Stassforth deposits were mainly responsible for the supply of the world's requirements of potassium salts before the war. This source of supply is now completely cut off; and potassium chloride sells to-day at the fancy price of Rs.200 a ton. We normally require about 200 tons of potassium chloride per year; but if the manufacture of potassium chlorate is undertaken in India at an early date, a cheap source of potassium chloride will be very welcome. There still lingers an export trade from India of about 7,000 tons of potassium nitrate which is mostly obtained from the efflorescent soils of

Bihar and the U.P. In the last Great War, it even paid to manufacture potassium carbonate from this nitre by ignition with saw-dust. The Pioneer Magnesia Works have just developed a process for the recovery of potassium chloride by evaporation of the bitterns from the salt wells at Khoragoda. It has been found that crystals of potassium chloride are obtained when the specific gravity of the bitterns lies between 31 and 34 Baume during the process of evaporation. Indeed they hope to make handsome profits by the exploitation of this source of supply of potash salts. It is interesting to note also that the possibility of recovering potash salts from molasses and from the ash of bagasse, which contains 4 and 11% potassium respectively, are under investigation by the Board of Industrial Research.

Nowhere is the interdependence of different industries better exemplified than in the synthetic fertilizer industries of India. Prior to the growth of the sugar industry in India, ammonium sulphate was used only in the large plantations of India, e.g. tea. Within a few years of the adoption of a protective policy for sugar by the Government of India, the import of Java sugar practically disappeared, and Indian factories developed the capacity of producing about 1 million tons of sugar which is more than sufficient to meet the country's requirements. The import of ammonium sulphate to fertilize the sugar fields shot up during this period from 30,000 tons to 80,000 tons valued at about 85 lakhs of rupees at pre-war prices. Attempts have not been lacking in India to make ammonium sulphate. The growth of the iron and steel industry has resulted in the distillation of $3\frac{1}{2}$ million tons of coal to produce metallurgical coke. For lack of demand, however, the by-products of the coke ovens are not completely utilized. Three and a half million tons of coal are capable of yielding about 50,000 tons of ammonium sulphate, but the actual production from this source is only 18,000 tons. The cost of manufacture of sulphuric acid in India is the chief handicap; and it is oftentimes not a paying proposition to absorb the ammonia of the coke oven gases with sulphuric acid and produce ammonium sulphate. The Mysore State has often pursued with success the policy of self-sufficiency, and with commendable vision put up, just before

the war started, a plant for the manufacture of synthetic ammonia and sulphuric acid. The factory is expected to produce every year 6,000 tons of ammonium sulphate which is necessary to fertilize the cane sugar fields in the Irwin Canal area. Due to war, however, it is probable that a large part of this synthetic ammonia will be converted into nitric acid by oxidation; and schemes are afoot to double the production of synthetic ammonia by this plant. I have already referred to the handicap from which the industry of synthetic fertilizers in India suffers due to lack of cheap sources of sulphur. In Germany where sulphur is not available within the borders of the country, ammonium sulphate is now mostly manufactured from ammonia, gypsum, and carbon dioxide. Under the auspices of the Board of Industrial Research, investigations are now in progress regarding the suitability of Indian deposits of gypsum as raw material for the manufacture of ammonium sulphate.

Fifty per cent of the world's huge production of sulphuric acid is used up in conversion of rock phosphate to superphosphate which makes the phosphorus available as plant food. In South India, bone ash is used in place of rock phosphate, and Messrs. Parry & Co. manufacture annually about 2,000 tons of phosphatic manures from this source. In recent years, the deposit of phosphatic nodules in the Trichinopoly area has been carefully surveyed and representative samples from this extensive deposit are found to contain 61% calcium phosphate. The problem of the conversion of such rock phosphate into a form which can be utilized by the plants, by processes which are not dependent on sulphuric acid, has engaged the attention of industrial and agricultural chemists for a long time. It has been claimed that treatment of very finely divided rock phosphate by steam at high temperatures may yield the desired result. This problem is being thoroughly investigated now in the Indian Institute of Science.

From this general review, it is clear that the heavy chemical industries in India may soon satisfy a large part of the country's requirements. At least the position is not so desperate as it was in 1914. It is an entirely different tale when we consider the dyestuff industry. The import of dyeing and tanning materials in India

amounted to 3.9 crores of rupees approximately in 1937-38. Out of 2.3 million lb. of alizarian dyes imported into the country, Germany supplied 1.4 million lb.; of the total import of 18.6 million lb. of other coal-tar dyes, Germany supplied 13.5 million lb. In September 1939, the Indian Mill Owners' Association had laid by considerable stocks of dyestuffs in anticipation of war, and also the stock of German dyestuffs in Bombay, which was confiscated as enemy property, was found to be of very considerable magnitude. Just at the present moment, therefore, the stream of supply of dyestuff has thinned down but has not dried up. If, however, the contingency were to arise, that maritime communications with Great Britain were seriously dislocated, practically all the dye-houses in India would have to close down. The history of the British dyestuff industry should be an object-lesson to us in our present position. Before the last war, Great Britain did not possess a dyestuff industry of any importance, over 90% of the dyes used being imported from Germany. As the last Great War progressed, the situation became very serious, and it was realized that the British dependence on Germany for dyes was tantamount to a much wider and more fundamental weakness of British chemical industry, as the production of dyes was intimately connected with the production of chemicals in general. Modern war depends for its successful prosecution on an abundant supply of an infinite variety of chemicals; and a dyestuff and fine chemical industry must be considered an integral part of every defence programme. Having realized the vital necessity of the development of a dyestuff industry, the British Government took immediate and far-reaching steps in this direction. Beginning with a direct and large subsidy for the formation of a new company, millions were spent on the rapid development of every branch of the industry. Later on, the importation of dyes and even intermediates was prohibited, except under licence for special reasons. As a result, the British dyestuff factories are now producing over 90% of their home requirements and have in addition a considerable export trade. Military authorities in India are now considering seriously the defence problems that would arise if supply of war materials were cut off from Great Britain. In

addition to such considerations, it should be always remembered that textile is our primary industry. The immediate establishment of a dyestuff industry is, therefore, a matter of such urgent necessity that the fullest resources of the State and the individual must be mobilized for the purpose.

The textile industry requires, besides dyeing, bleaching, and other auxiliary agents, various kinds of sizing materials, chief of which are magnesium salts and starch. As regards manufacture of magnesium salts, the industry is practically standing on its own legs, and it is probable that an export trade may be developed during war-time. The fate of the starch industry reveals the difficulties that a modern industry has to face, and the advantages it can secure, because of competitions and dislocations respectively in international trade. We had a few small starch-making factories in Northern India, when Birla Brothers put up a big factory two years ago at Rangoon. It was intended to produce starch from the maize and rice grown in abundance in Burma. The American Corn Products Corporation which controls the market for such types of starch immediately brought down prices in India, and the starch factory at Rangoon practically ceased production. The war, however, came as a godsend, and the factory is now working more than full time. Starch from potatoes, known as Farina, was supplied before April 1940 by Holland both to England and to India; and now this supply has been completely cut off. If enterprising manufacturers can now produce this commodity from Indian potatoes, they can not only capture the Indian trade but also set up a profitable export trade with the United Kingdom.

What is true of the synthetic dyestuff industry is also true of the synthetic drug industry in India. Considerable progress has been made in the manufacture of pharmaceutical preparations, sera and vaccines, and a national self-sufficiency as regards these materials may be easily attained in India. But even such common synthetic drugs as aspirin, atebirin, veronal, sulphanilimide derivatives, salvarsan, etc. are not produced in India. A fine chemical industry, a synthetic dyestuff industry, and a synthetic drug industry—they all go hand in hand. Where one fails, the others are bound

to falter; and measures for the protection of one, mean also measures for the protection of the others. They can be built up only on the sure foundation of a coal-tar distillation industry.

The nucleus of the industry already exists in the country. As stated before, $3\frac{1}{2}$ million tons of coal are being distilled now for the manufacture of metallurgical coke. All that is needed is that the coke oven factories should be encouraged by suitable protective measures to recover the ammonia and benzole and distil the tar. There is more demand in India for ammonia as ammonium sulphate than can be produced in the coke ovens; the high price of sulphuric acid is the only impediment to the development of this industry; and a protective import duty on ammonium sulphate should be imposed until such time as cheap sources of sulphur have been discovered and exploited in India.

Forty million gallons of crude benzole containing 68% benzene and 28% toluene can be obtained from $3\frac{1}{2}$ million tons of coal. A factory is being put up at Jamshedpur for the recovery of toluene which is essential for the manufacture of trinitrotoluene—the most important high explosive used in war. But for long time to come, this benzole cannot be expected to be all used up in the chemical industries of the country. By far the greater quantity of benzole recovered in any country is used for motor spirit; and this should be the case in India also. Such use would bring down our import of petrol from 100 million gallons to 60 million gallons per year, and remembering that we have to export gold now to maintain our trade balance, it would not be a bad proposition at all. In Great Britain, benzole has always enjoyed a preference equal to the amount of excise duty imposed on petrol. The Falmouth Committee, which was appointed by the Committee of Imperial Defence to examine the various processes for the production of oil from coal in Great Britain, have recommended that a preference of 8*d.* per gallon should be guaranteed till 1950 on all motor spirit produced from coal. If only the Government of India follow in the footsteps of the British Government in this matter, coal-tar distillation will be a flourishing industry in this country.

A third way of stabilizing the coal-tar distillation industry is to follow a progressive policy of road improvement and road development in the country. It is estimated that there are 100,000 miles of motorable roads in India. It is very desirable that their tyre-destroying dusty surfaces should be given a smooth dressing of indigenous road tar within the shortest period possible. If such a plan for improvement of existing roads is carried through vigorously, the processing of the coal-tar will be quite a paying proposition, and there will then be no dearth of creosote, naphthalene, etc. to supply the requirements of our potential dyestuffs and fine chemical industries.

A review in bold outline of some of the problems that face the chemical manufacturer at the present moment may stimulate interest in the subject. As one ponders deeply over these problems, one feels confident that India has a great industrial future. Her resources in raw materials and in man power entitle her to a front rank leadership in the field of modern economic enterprise. But in order to fulfil that destiny, the sons of the soil must learn to take advantage of the latest developments in science and technology, must be prepared to give up age-old habits of living and working, must determine to dare and to pioneer. And, they can do it all, if a scientific and rationalistic outlook pervades the national mind.

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THERMOCOMPRESSSION AND ITS INDUSTRIAL APPLICATIONS

By

C. VENKATA RAO

Introduction

Thermocompression, dealing with recompression of low pressure vapours to a state of higher thermal potential, is widely applied in the beet and cane sugar industries, in distilled water plants, in the evaporation of milk, fruit juices, and tanning materials, and in the heating of buildings and public bath installations. Hence a proper perspective of this important branch of knowledge would greatly enrich our technological outlook.

One pound of low pressure steam at 10 lb. per sq. in. gauge, when supplied to the calandria of an evaporator operated at atmospheric pressure, evaporates roughly one pound of water. Hence a pound of this steam having a total heat content of 1,160 B.T.U. gives rise to a pound of vapour with a total heat content of 1,150 B.T.U. itself condensing to water at 240°F. with a heat content of 208 B.T.U. To regenerate one pound of the original steam 952 B.T.U. have to be supplied to the condensed water at 240°F. But 10 B.T.U. are only required in the case of vapours given out from the evaporator at atmospheric pressure. Hence if a proper process can be devised, it would be highly economical if the conversion is effected with only 10 B.T.U. instead of 952 B.T.U. This process is called thermocompression. Technically it deals with the recompression of vapours to be raised from a state of lower to a state of higher thermal potential. Thermodynamically it is a reversed Carnot cycle.

The apparent high economy of this process is responsible for its rapid development. This conversion was sought to be effected

by means of (a) nozzles, (b) turbo-blowers, and (c) reciprocating pumps.

The first application of this principle is found in a patent by Pelletan in 1840. His apparatus, shown in fig. 1, works on the

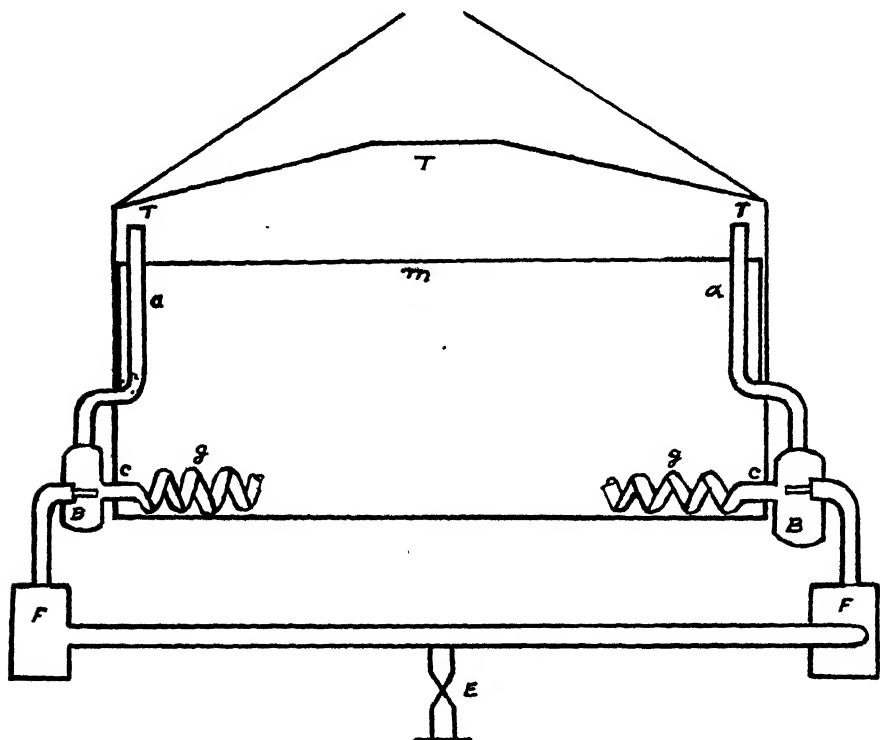


FIG. 1. Vapour Compression Apparatus of Pelletan.

principle of nozzle compression. The apparatus consists of a pan *m* with a cover *T* supplied by counter-weights. Heating is done by two coils *g*. High pressure steam is admitted by *E* and *F* to the injector nozzles *B*. These draw vapours from the pan through pipes *a* and compress them in the coils. This apparatus was not, however, a success probably due to faulty nozzle design and partly to the very low boiler pressures then employed.

Piccard-Weibel System

In 1879 the Piccard-Weibel system (25) came into considerable prominence and this embodies the principle of mechanical compres-

sion. Fig. 2 shows the system applied to a single effect evaporator. The reciprocating compressor C takes vapour from the dome A

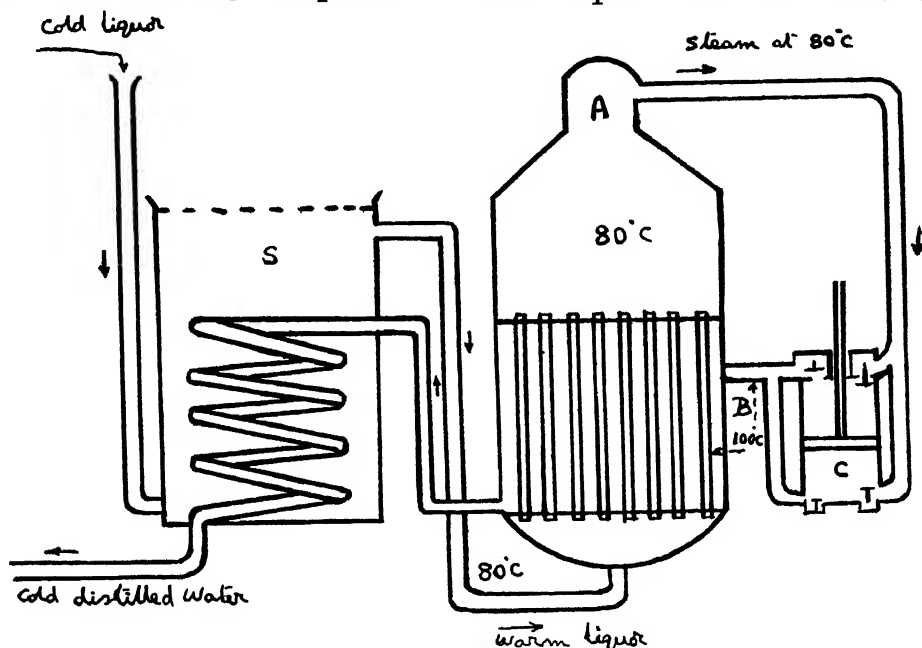


FIG. 2. Piccard-Weibel System.

and compresses it to be used in the steam space. This figure shows how clearly it was realized that in such installations heat must be saved, for the heat interchanger *S* is provided to heat the feed by the heat of the condensate. If the compressor *C* were to be steam-driven, the exhaust steam was best utilized in a triple effect evaporator as shown in fig. 3. This system was retained for a considerable

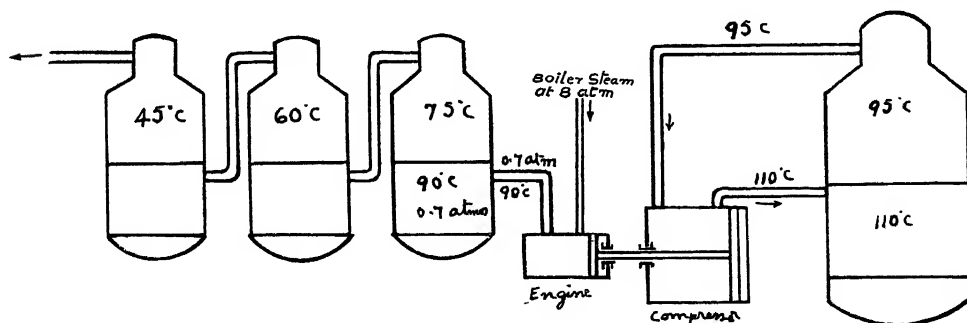


FIG. 3. Piccard-Weibel System using Compressor Exhaust.

time in salt works which had ample water power. But it never gained a foothold in the sugar industry because of the excessive size and the poor design of the reciprocating compressor.

For the success of a thermocompression unit, the pressure range through which the vapour is compressed must be small. Neglecting minor factors, this pressure range is made up of two parts, namely (a) the elevation in boiling point of the solution, and (b) the working temperature drop. The first part cannot be changed, but its effect may be minimized by confining the concentrated liquid to one part of the apparatus; for when an ordinary evaporator works continuously, the whole body is full of liquid at final concentration. On the other hand, the second factor is within the control of the designer; but the smaller it becomes the larger must the apparatus be for a given performance. If an evaporator could be designed with an unusually high coefficient of heat transmission, for a given duty, it could operate on a smaller temperature drop without the usual increase in size. Hence the features to be noticed in this and succeeding patents are (a) the isolation of the more concentrated parts of the solution, and (b) the attempts to increase the heat transmission coefficients.

Prache-Bouillon System

Prache and Bouillon (4, 13, 23) first developed the evaporator shown in fig. 4 embodying these improvements. Here the liquor space of an ordinary vertical tube evaporator is divided by partitions p which extend some distance above the upper tube sheet and also completely divide the liquor space below the tube sheet. Each compartment has its own downtake n and in the centre of each downtake is a pipe o leading to the next compartment. Thus a part of the liquid is continually being passed from one compartment to another, being finally withdrawn from 7. In this way the solution of the highest boiling point is localized in the last compartment and only a part of the heating surface is handicapped by this loss in temperature drop.

In this evaporator the steam space is not divided. Hence if the vapours are sufficiently compressed to give the desired working

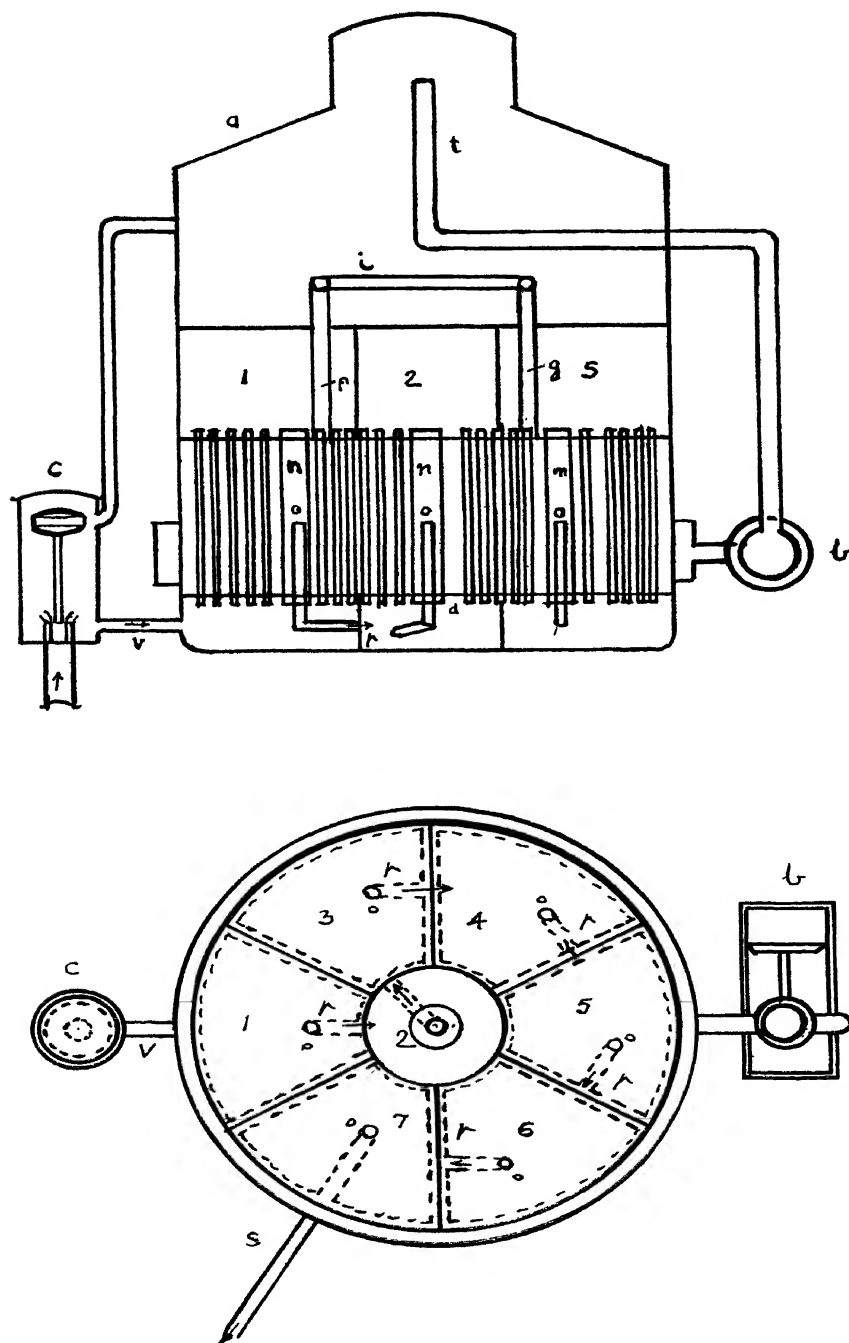


FIG. 4. Prache and Bouillon Vertical Tube Evaporator.

temperature drop for the dilute liquor, the compartments containing concentrated liquor will have a smaller temperature drop. But it is these compartments which need a larger working temperature drop than the others, because of the effect of increased viscosity and density of liquor on heat transmission coefficient. If, on the other hand, the vapour is compressed sufficiently to give a satisfactory working temperature drop for the last compartment, it will result in a range of compression too great to be economical for the others.

Turbo-Blower Developments

The other direction in which developments have taken place in thermocompression is the turbo-compressor. This is merely a rotor with vanes or blades fixed to it. It can be driven by an electric motor or a steam-driven turbine. The efficiency of this type of device is a little less than that of a reciprocating compressor. But it can handle much larger volumes in a comparatively smaller space. Besides, its action is continuous and hence a uniform delivery is assured without the use of a large receiver. Above all these, the most important advantage of the turbo-compressor is the absence of internal rubbing parts and internal lubrication. As a result, the heat transfer coefficient is higher with the compressed vapours from a turbo-blower, due to the absence of oil in these vapours. So it is used extensively in preference to the reciprocating type in spite of its lower mechanical efficiency. The combination of a turbo-compressor and an evaporator has been variedly described as 'Auto-evaporator' and 'Heat Pump'.

Among the various patents taken for mechanical compression by turbo-blowers those of Soderlund and Boberg (1, 26) are of considerable importance and are assigned to the Techno-Chemical Laboratories Ltd. (London, 1917). They have attempted both to isolate the effect of boiling point elevation and to get a higher heat transfer coefficient. The latter has been accomplished in their patents by promoting film evaporation. In the evaporator shown in fig. 5, a high coefficient is supposed to result from liquor trickling down the sides of the tubes, distribution being made through the device *i* hung in the tops of the tubes. Feed being preheated by

condensate entering at *d*, goes to chamber 2 and is circulated by pump 4 to chamber *h*. Vapours are withdrawn from *K*, compressed by

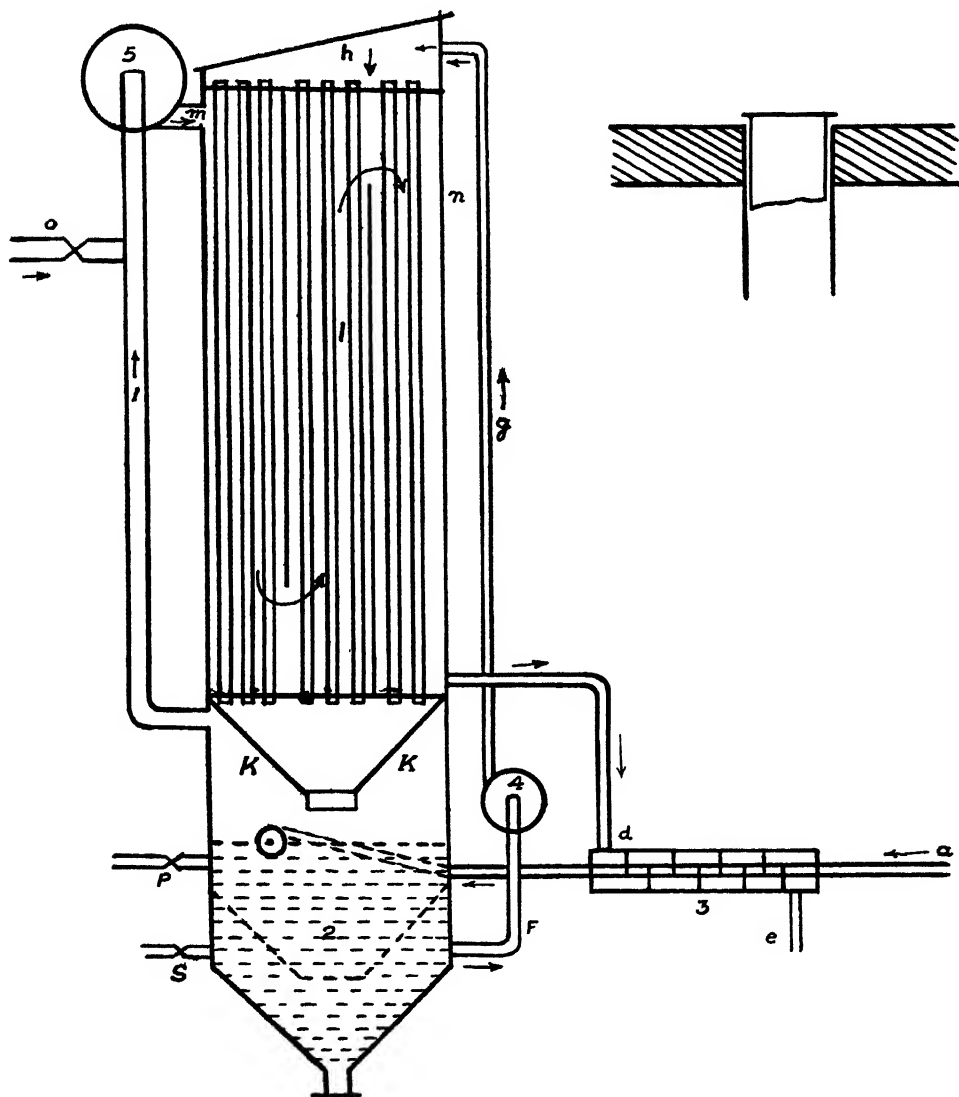


FIG. 5. Vertical Soderlund-Boberg Evaporator.

blower 5 and returned to *m*. With a modification of this design but adhering to the same principles, high coefficients are obtained

by showering the liquid over horizontal tubes somewhat as in the Lillie Evaporator and at the same time an isolation of the effect of boiling point is obtained by running a series of bodies, vapour being stepped up by intermediate turbo-blowers to give a working temperature drop and also to overcome the elevation in boiling point of the liquid. The patent claims expressly call for a working temperature drop of not over 3°C . (5.4°F .). Hence some type of film evaporator must be used; otherwise hydrostatic head would use up all the available drop. The patent covers the same principle applied to vertical evaporator.

The success of a thermocompression system using turbo-blowers is assured if cheap hydroelectric power is available. In this case power should be available at a figure very much under the cost of generation in the plant to make the compressor arrangement economical.

Nozzle Compressor, its design and performance

The vapours in this case attain a higher thermal potential in a nozzle, the actuating medium being high pressure boiler steam. In this field the first successful commercial installation was made by Prache et Bouillon, of Paris, who in 1905 developed a steam jet nozzle which was claimed to be far superior to any other then in existence.

In 1918 de Baufre (11) at Annapolis developed a nozzle as applied to evaporators. In ordinary operation high pressure steam is expanded through an orifice and a nozzle tube. Vapour from the evaporator is drawn in through the inlet and the mixture of compressed vapour and expanded high pressure steam is discharged to the evaporator coils.

The performance of the nozzle has been the subject of a considerable amount of study. Erdlencher (13) has reported data on the performance of Prache and Bouillon nozzle which was installed at the beet sugar factory at St. Lew d' Esserent in France. He states that the first effect of the multiple effect evaporator uses steam at 3.9 lb. per sq. in. gauge pressure and boils at atmospheric pressure. The live steam used in the thermocompressor is at 120 lb.

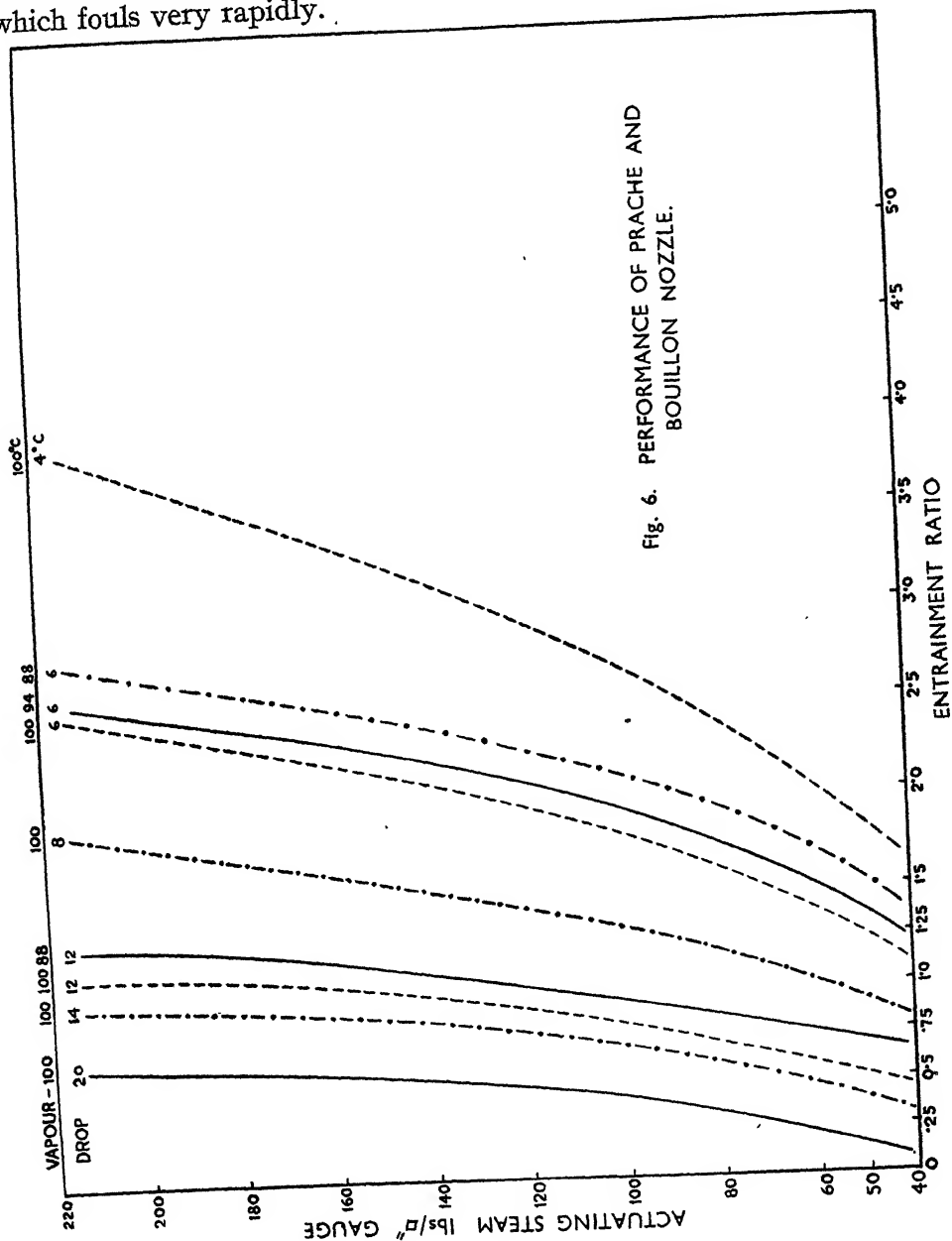
gauge. One pound of this aspirates and compresses rather less than two pounds of steam from the vapour space of the first effect. The single effect will then operate as a triple and in a triple effect evaporator each pound of live steam will operate at quintuple and each pound of exhaust at triple effect efficiency.

The experimental data of Erclencher is presented in the graph of fig. 6. It gives the ratio of pounds of vapour to pounds of high pressure actuating steam for different steam pressures, vapour temperatures, and temperature drops. It will be noticed from the graph that the capacity of the nozzle falls off very rapidly as the working temperature drop increases and as the pressure range, through which the high pressure steam is expanded, decreases. So it is necessary for successful operation to maintain the working temperature drops within 10°C .

For obvious reasons the limits of vapour compression are well defined and success depends upon the selection of conditions favourable to their application. The temperature drop being small, these installations are limited to the concentration of low density and easy boiling solutions of low viscosity. The successful range of operation will be at atmospheric pressure or above it, as low pressures result in large specific volumes with the consequent frictional losses due to the higher vapour velocities. It is for this reason that in all the sugar factories the thermocompression unit is usually mounted to the first body of a multiple effect evaporator.

These thermocompressors should not be installed on evaporators where the difference of pressure between the two sides of the heating surface is subjected to considerable fluctuations, as the nozzles are designed to operate under a given set of pressure conditions and these will become less efficient under altered conditions. In adverse conditions the nozzle compressor will cease to work and actually 'back fire' when the actuating steam will flow back on itself, not having sufficient mass velocity to overcome the back pressure under the nozzle proportions. If this pressure difference is increased, the ratio of compression decreases rapidly. Hence it is essential to install the compressor on a body which does not foul under working conditions. The one which gives least trouble and

is very satisfactory from this point of view is the vapour cond. However, it would be bad practice to install it on a Pauly pre-evaporator which fouls very rapidly.



If the amount of make-up steam required is variable, the nozzle will give useful results only when the throttle valve is wide open. Under conditions demanding less than the maximum amount of make-up steam, its capacity will be negligible. This has been discussed by Classen (7) and several others who suggest several small nozzles in parallel to be cut in one at a time as the demand for make-up varies, but each to be either completely closed or wide open, but never throttled.

Heat Pump

Thermocompression systems in the name of 'Heat Pump' (6, 9, 26, 29) manifest themselves in fields other than evaporation. Recently Haldane (1930) discussed its application to the heating of buildings and public baths and he gave estimated figures for a public bath installation.

The thermodynamic efficiency of Carnot cycle is given by $\frac{T_1 - T_2}{T_1}$, where T_1 and T_2 are the absolute temperatures of the source and the sink. In the case of 'Heat Pump' heat is absorbed from a cold source and rejected to the hot source by the expenditure of mechanical energy. Hence it is a reversed Carnot cycle and its efficiency $\eta = \frac{T_1}{T_1 - T_2}$. The greatest efficiency is obtained when $T_1 - T_2$ is as small as possible. This restricts its application to low temperatures. If $T_1 - T_2$ is small compared to T_1 , a small amount of mechanical work supplied by a blower or a pump will allow a very much larger amount of heat to be pumped from the cold to the hot source.

If heat is delivered at 100°F. and taken in from the atmosphere at 40°F., the theoretical efficiency would be $\frac{560}{560 - 500} = 9.33$. That is to say, for every B.T.U. of electrical energy put into the heat pump 9.33 B.T.U. will be delivered at a temperature of 100°F. and as each B.T.U. of electrical energy may have required the consumption of 5 B.T.U. (20% efficiency) at the power station, the remarkable fact is revealed that it is at least theoretically possible for the

consumer of the electrical energy, produced at the generating station, to obtain considerably more heat than is required to produce the electrical energy which he consumes. This process brings about an economy in fuel consumption as compared with direct conversion.

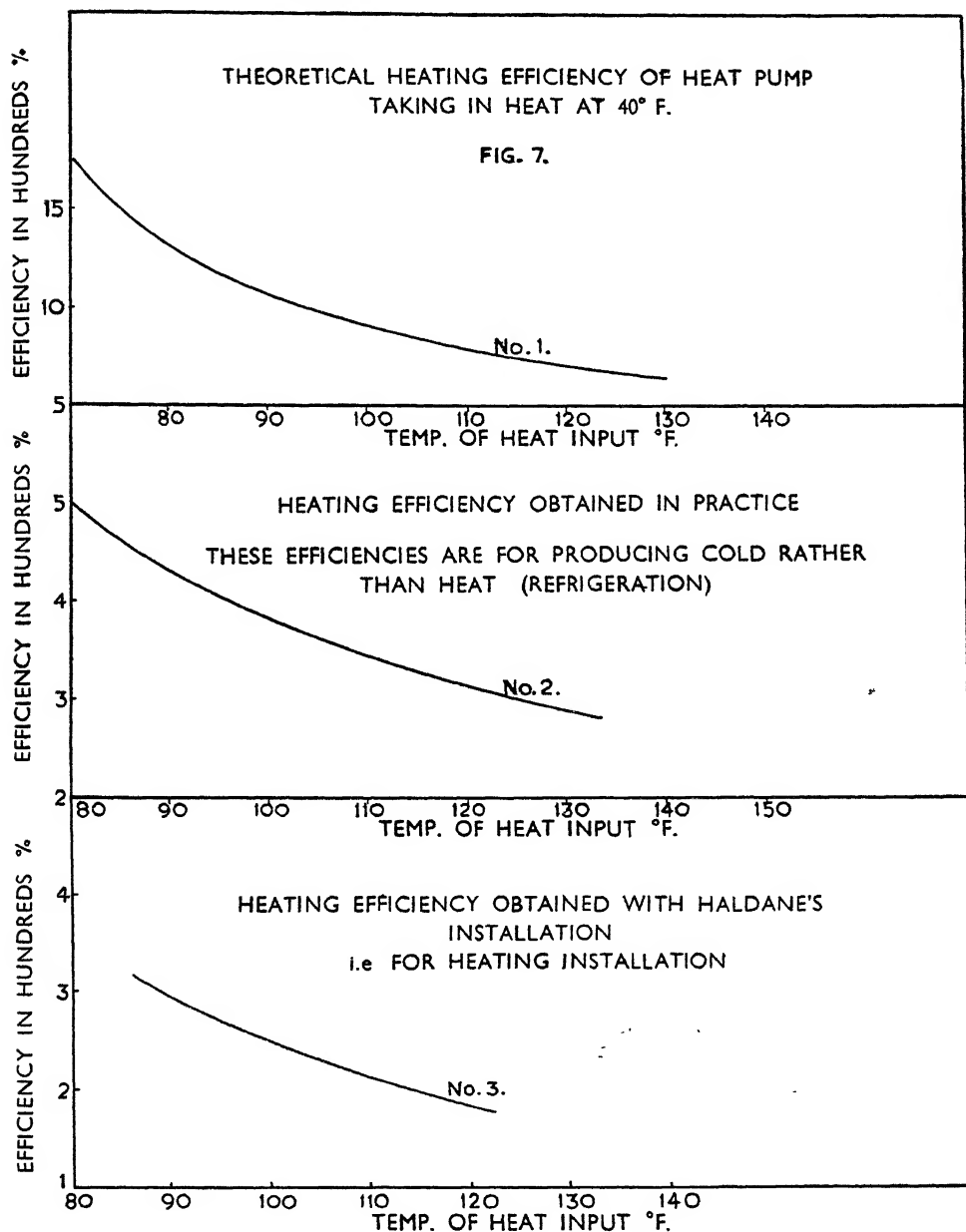
The general principle of this process was first pointed out by Lord Kelvin in 1852 (his collected papers, Vol. I, p. 515) working on this principle. Haldane (17) remodelled a small refrigerating plant using ammonia as the working fluid to heat a house and obtained very satisfactory results. Using large radiators working at 100°F. efficiencies of 200% to 300% were obtained. His results are shown in the graphs (fig. 7). Graph 1 gives the theoretical efficiency of a heat pump absorbing heat at 40°F. and delivering it to a hot source at different temperatures. Graph 2 represents the efficiency obtained in refrigerating machines which, though based on the above principle, are intended to produce cold rather than heat. Graph 3 gives the efficiencies obtained by Haldane on his experimental heat pump installation.

These results of Haldane clearly demonstrate the successful application of thermocompression systems to the heating of buildings and public bath installations.

Summary

Nozzle compression systems are employed in the evaporation of beet and cane juices and in salt works. These work successfully for small temperature drops (5 to 10°F.) at atmospheric pressure. It is noticed that the efficiency of the nozzle falls off very rapidly with increased temperature drop. The application of turbo-blower compression systems proves particularly advantageous (*a*) when objectionably high pressures would be required in the first stages of multiple effect operation; (*b*) when low and constant temperatures are required by the nature of the solutions being handled; (*c*) when the boiling point elevation with concentration is small; and (*d*) where there exists a use for exhaust steam whose temperature can be made independent of the evaporation temperature.

Among the various thermocompression systems turbo-compressors can handle large volumes of vapours over a small range of



temperature drop, but are unsuitable for handling small volumes. Nozzle compressors are the best for dealing with small volumes; but they give a surplus of vapour which has to be condensed or disposed off otherwise.

At present greater attention is being focussed to the application of thermocompressors in the name of heat pumps to systems other than evaporation. Haldane has clearly demonstrated its successful application to the heating of buildings and public bath installations.

BIBLIOGRAPHY

1. Anon. J.S.C.I., 1917, 36, 70.
2. Anon. Am. Sug. Ind., 1911, Vol. 13, p. 538.
3. Andes, L. E. Kunststoffe, 1921, 11, 74 and 83.
4. Badger, W. L. Chem. Met. Eng., 1923, 28, 26 and 73.
5. Bianchini. Giorn. Chem. Ind. Applicata, 1922, 5, 219.
6. Carlsson, G. Chem. Met. Eng., 1921, 26, 645.
7. Classen, H. Z. ver. deut. Zuckerind., 1902, 52, 781.
8. " " " " 1921, 71, 440.
9. " " " " A. angew. Chem., 1921, 34, 223.
10. Cunze. Z. ver. deut. Zuckerind., 1882, 32, 541.
11. de Baufre. J. Am. Soc. Mech. Eng., 1918, 40, 746.
12. Dunglinson. Chem. Met. Eng., 1921, 25, 246.
13. Erclencher. J. Faber. Sucr., 1911, sept 13 (sec. 2).
14. Flügel. Z. ver. deut. Ing., 1920, 64, pp. 954 and 986.
15. Gensecke. Chem. Met. Eng., 1932, 28, 448.
16. Gonzaliz. Facts about Sugar, 1931, 27, 69.
17. Haldane, T. G. N. J. Inst. Elec. Eng. (London), 1930, 68, 666.
18. Heucke. Centr. Zuckerind., 1926, 34, 664.
19. Holmes. Paper Maker and Paper Trade Jour., 1922, p. 610.
20. Jörn, K. Centr. Zuckerind., 1926, 34, 785.
21. Koerting. Z. ver. deut. Zuckerind., 1874, 24, 527.
22. Ombeck. Z. ver. deut. Ing., 1921, 65, 64.
23. Prache and Bouillon. Bull. Asson. Chem. Sucr. Dist., 1923, 41, 147.
24. Pridgeon, L. A. Chem. Met. Eng., 1923, 28, 1109.
25. Schaeffer and Budenberg. Z. ver. deut. Zuckerind., 1879, 29, 1015.
26. Schroeder. Chem. App., 1915, 2, 210.
27. Schulz. Chem. App., 1933, 20, 51.
28. Tromp, L. A. Int. Sug. Jour., 1935, 37, 386.
29. Wigginton. Fuel in Science and Pract., 1930, 9, 293.
30. Wirth. Z. ver. deut. Ing., 1921, 65, 1183.
31. " " " " 1922, 66, 160.
32. Badger, W. L. Heat Transfer and Evaporation, 1st Edition, 1926, 175-8.
33. Deer. Cane Sugar, 2nd Edition, 1921, 354-6.
34. Schüle. Technical Thermodynamics, 1st Edition, 1933, pp. 564 and 569.
35. Tromp, L. A. Machinery and Equipment of the Cane Sugar Factory, 1st Edition, pp. 456-62.
36. Webre and Robinson. Evaporation, 1st Edition, 1926, pp. 93 and 287-9.

NEW ASPECTS OF NITROGEN FIXATION AND NITROGEN LOSS IN SOILS

By

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S. K. MUKHERJI

Nitrogen, though it ordinarily exists in the inactive form in air, is highly important in the combined state both in war as a source of explosives and in peace as a fertilizer for the soil.

The low yield 8 to 10 maunds of wheat per acre in India as compared to 25 to 26 maunds produced per acre in Belgium and other countries is due chiefly to the nitrogen deficiency of Indian soils and lack of artificial manures. The low yield of cane sugar from Indian soil as compared to the other sugar producing countries of the world is also due to the same cause. Every civilized nation,

TABLE I
Nitrogen fixed in tons (1937)

Country	Plants	Quantity
Germany	13	13,65,850
Japan	21	4,90,132
U.S.A.	10	2,92,510
France	27	2,44,050
England	2	2,32,870
Belgium	10	2,17,980
Soviet Union	4	1,57,500
Italy	18	1,46,830
Holland	3	1,36,630
Norway	4	1,21,000
Canada	3	1,02,000
Manchuria	1	40,000
Sweden	3	14,000
Switzerland	3	13,200
Spain	2	8,000
China	2	7,175
South Africa	1	5,740
Hungary	1	5,740
TOTAL	35,47,352 tons.

therefore, has its own nitrogen fixation industry and the production of combined nitrogen may rightly be taken as a measure of the standard of civilization. The nitrogen industry today is almost as important as the steel or the coal industry. Germany stands at the top, while Japan is only second to it. Unfortunately, India has no such industry (vide Table I). Recently a nitrogen fixation factory has been started in the Mysore State.

The amount of nitrogen necessary for the production of a single good crop from an acre of soil is about 25–50 lbs., because this is the amount actually present in the crop and the hay. However, even in civilized foreign countries the actual amount of nitrogen supplied in the form of artificial manure is much less than the requisite amount. (Table II.)

TABLE II
Pounds of Nitrogen used per acre of land under cultivation

Country	Nitrogen added per acre per year in pounds		Country	Nitrogen added per acre per year in pounds	
Holland	..	24.79	France	..	4.0
Belgium	..	28.55	Italy	..	4.29
Germany	..	15.65	Great Britain	..	2.49
Denmark	..	10.26	United States	..	1.36
Norway	..	5.98	Poland	..	0.73
Sweden	..	5.24	Hungary	..	0.15

In India no such artificial manure is supplied; and yet every year the soil yields a fair crop. It is clear, therefore, that we must account as to how the soil makes up this deficiency of nitrogen.

Nitrogen of the air is usually fixed as ammonia by the Haber-Bosch process. This important discovery was responsible for making Germany independent of other nations and thus enabled it to face the Allies during the last Great War. The ammonia is easily oxidized to nitric acid, which is the life-blood of a nation at war.

The other method of fixing nitrogen of the air is due to Birkeland and Eyde and others, in which nitric oxide, which is first formed is finally converted into nitrous and nitric acids. The reaction



requires energy 43.2 Kilo-calories. This is supplied in the form of electrical energy. The amount of electrical energy actually utilized is approximately 1 to 2% of the total supply and therefore this is a wasteful process of fixing nitrogen even when electric energy is cheap.

Nernst¹ and co-workers showed that with a high tension alternating current arc the following results were obtained:—

Temperature ..	1538°	1604°	1760°	1922°	2307°	2402°
x { Obs. ..	0.37	0.42	0.64	0.97	2.05	2.2
{ Calc. ..	0.35	0.43	0.67	0.98	2.02	2.3

where x denotes the percentage of nitric oxide by volume at equilibrium, starting with air containing 79.2% of nitrogen and 20.8% of oxygen, $x^2 = K(79.2 - \frac{1}{2}x)$ in the reaction $N_2 + O_2 \rightleftharpoons 2NO$, i.e. $[O_2] [N_2] K = [NO]^2$.

The only conclusion that could be drawn from the close agreement between the observed and calculated values of x is that the reaction is solely produced by the absorption of heat, and there is no deviation from the law of mass action due to special electrical effects. Förster² and others found that the yields of nitric oxide were practically identical with the direct and alternating current discharges and hence concluded that the reaction in the arc is not affected by electrical influences, but is purely a thermal process.

Haber³ and co-workers obtained larger yields of nitric oxide than were obtained by Nernst. Thus, while Nernst obtained 5% of nitric oxide at 3200°, Haber and König observed that the percentage amount of nitric oxide formed increased with current density up to a maximum and then it is not affected by a further increase of current density. They experimented with pressures varying from 40 to 200 mm. The greatest yield of nitric oxide was obtained at 100 mm. pressure and the values are as follows:—

Oxygen originally present ..	20.9	48.9	44.4	75.0	81.7%
Nitric oxide produced ..	9.8	14.4	14.3	12.77	12.1%

Hence it is believed that some influence other than the purely thermal change represented by the equilibrium $N_2 + O_2 \rightleftharpoons 2NO$ must be at work. Berthelot and Gaudechon⁴, Warburg⁵ and others have proved that nitric oxide is produced by the silent electric

discharge in the air at ordinary temperatures when the thermal equilibrium virtually corresponds with no formation of nitric oxide. Hence E. Warburg⁶ has concluded that the formation of nitric oxide in the arc cannot be a purely thermal process. The electric equilibrium was believed to be dominant only when the temperature is low enough to decompose the nitric oxide very slowly. It was stated that while the thermal equilibrium is determined only by the law of mass action and temperature, the electrical equilibrium is also affected by the amount of electrical energy spent per unit of time and this also determines the difference between thermal and electrical equilibria. Haber was to realize this condition experimentally by passing the gases slowly under diminishing pressure through narrow tubes completely filled by the arc and cooled by a water jacket. The yield of nitric oxide was much higher than that corresponded with the simple thermal equilibrium at the temperature of the arc. It was argued that the use of a low temperature arc gives better results than a high temperature arc, although this arc has not yet been industrially worked out.

The reason why Nernst and co-workers obtained results in agreement with purely thermal equilibrium when working with a high tension arc is the rapid secondary thermal decomposition of the nitric oxide. The thermal influence got the upper hand of the electrical. F. Fischer and E. Hene⁷ suggested that the apparent deviations from the mass action law observed by A. Grau and F. Russ⁸ and the high concentration of nitric oxide obtained by Haber and co-workers with the cooled arc are due to the activation of the oxygen in the electric arc.

There is another explanation of this increased yield of nitric oxide in the arc and it may be attributed to the absorption of the light by the reacting system. It seems quite probable that the light energy absorbed by the system leads to a greater yield of nitric oxide. This view can be tested by exposing the system to strong light from an external source.

It should be remembered that it is not necessary that the energy required for nitrogen fixation should be supplied as electrical energy. It may be supplied as chemical energy and even then

the fixation of nitrogen should be possible. The oxidation of glucose (sugar) gives out a large amount of energy about 676 Kilo-calories per 182 grams of glucose. This is several times greater than the energy required for nitrogen fixation as nitric oxide. Hence if glucose or any other carbohydrate or any substance, which on oxidation produces sufficient amount of energy, is added to the soil, the nitrogen and oxygen of the air will be fixed on its surface. Not only this, but the fixation is more in the light than in the dark, because in the light in addition to the chemical energy there is solar energy which is also utilized for fixing nitrogen.

The increased fixation in light is not due to an increase in the number of Azotobacter bacteria which can fix nitrogen in soil; actual measurements have shown that their number is much less in the light than in the dark. Hence the increased fixation must be due to solar energy. This is further confirmed by experiments on sterile soil, which contains no bacteria, and yet the nitrogen fixation is greater in the light than in the dark when the soil is mixed with sugar or energy material.

The presence of cellulose, plant residues, molasses and other carbonaceous matter is highly essential for nitrogen fixation. Molasses contains a large percentage of cane sugar and glucose, which on oxidation liberate chemical energy and fix the atmospheric nitrogen in the soil. India produces about 1,000,000 tons of molasses per year and its disposal is a great problem. Its utilization as a manure to fix nitrogen is therefore of very great significance when the supply of artificially fixed nitrogen from outside may be stopped due to the war. The addition of cowdung to the soil not only supplies its nitrogen to the soil, but by the oxidation of its carbonaceous matter (cellulose, pentosan, etc.) fixes additional nitrogen.

From Table II on p. 68, it will be seen that the nitrogen supplied to the soil as artificial manure though much less than the actual quantity required for a single crop we obtain a fair crop year after year from the same soil because the deficiency is made up by the natural process of fixing nitrogen from the air with the help of the chemical energy produced by the oxidation of carbonaceous matter that remains or is supplied to the soil. On

the top of this there is the solar energy which also helps a great deal in fixing the atmospheric nitrogen. Hence the nitrogen need of plants all over the world is mostly met through the agency of sunlight, which helps nitrogen fixation and causes the formation of carbonaceous compounds, required for nitrogen fixation.

The amount of nitrogen fixed in the soil on the addition of energy rich materials is always nearly double the amount fixed in the dark, though the number of bacteria is predominantly larger in the latter. The following results were obtained in fields and in dishes:—

FIELD TRIALS

Plot 4 ft. by 4 ft. containing 10 kilograms molasses

(Exposed)

Date	NH ₃ -N%	NO ₃ -N%	Total nitrogen %	Total carbon %	Azotobacter per gram of dry soil in millions	Total bacteria per gram of dry soil in millions
13-2-1937 (original soil)	0.0006	0.0014	0.0310	0.3472	0.9	12.0
9-3-1937	0.0012	0.0016	0.0344	1.7708	12.5	38.0
26-4-1937	0.0016	0.0016	0.0388	1.4136	75.0	245.0
12-7-1937	0.0028	0.0016	0.0456	0.6874	155.0	385.0
25-9-1937	0.0019	0.0017	0.0461	0.4728	115.0	305.0

Nitrogen fixed per gram of carbon oxidized = 8.9 mgm.

(Dark)

13-2-1937 (original soil)	0.0006	0.0012	0.0300	0.3240	1.0	13.0
9-3-1937	0.0010	0.0015	0.0328	1.7732	16.0	48.0
26-4-1937	0.0013	0.0015	0.0344	1.4702	120.0	365.0
12-7-1937	0.0014	0.0015	0.0375	0.7854	290.0	615.0
25-9-1937	0.0013	0.0016	0.0388	0.4468	315.0	645.0

Nitrogen fixed per gram of carbon oxidized = 3.56 mgm.

Plot 4 ft. by 4 ft. containing 4 kilograms starch

(Exposed)

Date		Total nitrogen %	Total carbon %	Moisture %	Azotobacter per gram of dry soil in millions	Total bacteria per gram of dry soil in millions
13-2-1937 (original)	..	0.0311	0.3374	1.5	1.5	13.5
12-3-1937	..	0.0333	1.0622	3.0	6.5	26.0
27-4-1937	..	0.0365	0.8618	4.0	48.0	140.0
24-5-1937	..	0.0388	0.7442	3.0	75.0	195.0
10-6-1937	..	0.0407	0.6702	3.5	70.0	210.0
11-7-1937	..	0.0424	0.5594	..	76.0	215.0
29-9-1937	..	0.0411	0.4684	4.0	35.0	175.0

Nitrogen fixed per gram of carbon oxidized = 16.5 mgm.

(Dark)

13-2-1937 (original)	..	0.0420	0.4360	1.5	1.5	13.5
12-3-1937	..	0.0437	1.1924	4.0	8.5	31.5
27-4-1937	..	0.0456	1.0214	4.0	70.0	205.0
24-5-1937	..	0.0462	0.9258	3.5	105.0	245.0
10-6-1937	..	0.0466	0.8205	4.5	130.0	282.3
11-7-1937	..	0.0472	0.7036	4.0	165.0	345.0
27-9-1937	..	0.0482	0.4864	4.8	162.6	350.8

Nitrogen fixed per gram of carbon oxidized = 5.9 mgm.

EXPERIMENTS IN DISHES

1 kilogram soil + 20 gms. Dextrin (Temp. 34°-40°)

(Exposed)

Date		Total nitrogen %	Total carbon %	Azotobacter per gram of dry soil in millions
8-10-1936 (original soil)	..	0.0570	0.6156	5.2
10-12-1936	..	0.0608	1.1926	17.2
18-1-1937	..	0.0636	0.9414	28.5
4-2-1937	..	0.0646	0.7728	20.5
20-2-1937	..	0.0640	0.6292	18.5
6-3-1937	..	0.0636	0.6086	11.5

Nitrogen fixed per gram of carbon oxidized = 13.03 mgm.

(Dark.) (Temp. 28°-31°)

8-10-1936 (original)	..	0.0570	0.6156	5.2
10-12-1936	..	0.0586	1.2644	32.5
18-1-1937	..	0.0600	1.1032	150.5
4-2-1937	..	0.0604	0.9778	198.5
20-2-1937	..	0.0608	0.8454	225.0
6-3-1937	..	0.0612	0.6868	280.0

Nitrogen fixed per gram of carbon oxidized = 5.98 mgm.

1 kilogram soil + 20 gm. Fructose

(Exposed.) (Temp. 34°-42°)

Date		Total nitrogen %	Total carbon %	Azotobacter per gram of dry soil in millions
8-10-1936 (original)	..	0.0570	0.6156	5.2
25-10-1936	..	0.0570	1.3568	6.1
1-12-1936	..	0.0608	1.1518	19.8
19-1-1937	..	0.0646	0.7614	29.8
5-2-1937	..	0.0656	0.6346	23.0
7-3-1937	..	0.0626	0.6126	10.5

Nitrogen fixed per gram of carbon oxidized = 11.9 mgm.

(Dark.) (Temp. 28°-31°)

8-10-1936 (original)	..	0.0570	0.6156	5.2
25-10-1936	..	0.0570	1.3745	7.2
1-12-1936	..	0.0590	1.2429	35.8
19-1-1937	..	0.0612	0.9876	225.5
22-2-1937	..	0.0618	0.7318	275.0
7-3-1937	..	0.0622	0.6126	290.0

Nitrogen fixed per gram of carbon oxidized = 6.8 mgm.

From the foregoing results it is quite clear that although the number of bacteria in the dark is many times larger than that in light, yet the amount of nitrogen fixation in soils, in plots as well as in dishes, is always nearly twice as great in light as in the dark. Moreover, the size of the colonies developed on the plates containing the incubated soil is much bigger than those obtained from the exposed ones. It appears, therefore, that the *Azotobacter* receiving sunlight is weakened. If bacterial metabolic activity is considered to go hand in hand with the growth activity, the fixation of atmospheric nitrogen in the incubated and dark basins should have been more than in the ones exposed if no other agent was responsible in nitrogen fixation. Therefore, in tropical soils *at least* along with bacterial fixation photochemical fixation seems to play a prominent rôle.

Nitrogen fixation has so far been considered to be entirely a bacterial process. But it is clear from the above set of results that nitrogen fixation in soils is markedly accelerated by light absorption and does not depend on bacteria alone.

Substance				Nitrogen fixed per gram of carbon oxidized	
				Light	Dark
Glucose (2%)	12.5 mgm.	6.5 mgm.
Glycerol (5%)	6.04 mgm.	2.76 mgm.
Starch (5%)	7.58 mgm.	3.13 mgm.
Mannitol (2%)	12.8 mgm.	6.9 mgm.
Dextrin (2%)	13.03 mgm.	5.98 mgm.
Fructose (2%)	11.9 mgm.	6.8 mgm.
Maltose (2%)	12.6 mgm.	6.5 mgm.
Galactose (2%)	12.09 mgm.	6.7 mgm.

Field trials

Glucose. (Plot 4 ft. by 4 ft. containing 5 kilograms glucose)	14.0 mgm.	7.26 mgm.
Molasses. (Plot 4 ft. by 4 ft. containing 10 kilogram molasses)	8.9 mgm.	3.56 mgm.
Starch. (Plot 4 ft. by 4 ft. containing 4 kilogram starch)	16.5 mgm.	5.9 mgm.

The above results show conclusively that for the same amount of carbon oxidized the nitrogen fixation in the light is much greater than that in the dark. Dhar and Mukherji⁹ have explained that the formation of nitric oxide may be the first step in the fixation of nitrogen. It is well known that the combination of nitrogen and oxygen forming nitric oxide according to the equation $N_2 + O_2 + 43.2 \text{ cal.} = 2NO$ is an endothermal chemical change which takes place when supplied with the required energy. When the energy materials are mixed with soil they undergo oxidation as is evident from the decrease of carbon with time. A gram molecular weight of these energy materials in their oxidation liberate energy much in excess of that required for the combination of nitrogen and oxygen forming nitric oxide. Even in the dark nitrogen fixation takes place in the soil when supplied with energy materials, but the efficiency of this process is low. When, however, the soils containing the energy materials are exposed to sunlight not only the velocity of oxidation of energy materials is increased as is evident from the quicker disappearance of carbon in light than in dark, but the efficiency of nitrogen fixation is also considerably increased. It seems therefore that nitrogen fixation, which is an endothermal reaction, is considerably aided not only by the energy obtained from the oxidation of the carbohydrates but also by the absorption of the incident light. As there is an intimate contact between the nitrogen and oxygen

on the soil surface, which is receiving energy both from the sun and from the oxidation processes, it is quite reasonable to expect more nitrogen fixation in the light than in the dark and this is actually observed experimentally. Hence we are led to conclude that light actually takes part in nitrogen fixation in the tropical soils.

In the case of starch and glycerol (5%) and molasses (10 Kg. in fields) the nitrogen fixed per gram of carbon is small when compared with others because of the high concentrations of the energy materials applied to the soil.

The following is the summary of results obtained at various temperatures on nitrogen fixation in the dark with soil and glucose incubated at different temperatures in thermostats. The result of the corresponding set in sunlight is also recorded for comparison:—

				Maximum number of Azotobacter per gram of dry soil in millions	Nitrogen fixed in milligrams
Temperature					
Dark	Exposed (42°)	22.5	13.1 mgm.
	10°-12°	6.0	nil
	25°	126.0	4.8 mgm.
	20°	175.0	6.4 "
	35°	200.0	7.76 "
	40°	98.0	3.97 "
	45°	78.0	3.03 "
	50°	7.5	1.6 "
	60°	nil	nil

From the foregoing results it is clear that the optimum temperature for nitrogen fixation in the dark is 35° as against about 28° (25°-30°) observed in temperate countries. Above and below this temperature the fixation is less. At 11° and 60° the fixation is nil. The nitrogen fixed in the exposed soil, the temperature of which varied from 40° to 44°, is much greater than that in the incubated soils. Under comparable conditions, the nitrogen fixed per gram of carbon oxidized when the soil is exposed to sunlight is always greater than the nitrogen fixed per gram of carbon oxidized in the dark at various temperatures, whereas the Azotobacter numbers in the exposed soil, are much less when compared to those in the soils incubated at temperatures 25°, 30°, 35°, 40° and 45°. In sunlight the nitrogen fixed is much greater than that obtained at the optimum

temperature 35°. This definitely proves that the increase of temperature in sunlight is not at all the factor responsible for the greater nitrogen fixation observed but is mainly due to the photo-oxidation of the energy-rich substances and energy added by light absorption. Therefore, photochemical fixation of atmospheric nitrogen is very important and light is as essential as bacteria in the process of fixation of nitrogen in tropical soils.

Recently we have carried on experiments under completely sterile conditions and in such cases also we have obtained fixation of nitrogen not only with sterile soils but also with surfaces like those of ZnO, Fe₂O₃, Al₂O₃, MnO₂, etc.

In the following experiments 50 gms. soil were taken to which 1 gram glucose was added.

The experimental arrangements are the same as before and the results are as follows:—

(1) *Soils in quartz flasks.* The following experiments were started on 12-9-1938

Analyzed on 1-3-1939 Analysis of the original soil					
			(Sunlight)	(Dark)	
			Total nitrogen	0.0424%	Total carbon
Substance	Total N	Total C	Total N
					Total C
Inulin	0.0464%	0.7732%	0.0424%
Arabinose	0.0448%	0.7904%	0.0424%
Fructose	0.0464%	0.7635%	0.0432%
Lactose	0.0456%	0.7816%	0.0424%
Glucose	0.0456%	0.7635%	0.0432%
Mannitol	0.0456%	0.7732%	0.0424%
Glycerol	0.0448%	0.8048%	0.0424%
Galactose	0.0456%	0.7732%	0.0424%
Maltose	0.0464%	0.7735%	0.0424%
Dextrin	0.0464%	0.7732%	0.0432%
Starch	0.0448%	0.9264%	0.0424%
Control	0.0408%	0.3986%	0.0416%

(2) *Soils in Pyrex flasks.* Analyzed on 27-3-1939

			(Exposed)		(Dark)	
			Total N	Total C	Total N	Total C
Substance				
Inulin	0.0456%	0.8968%	0.0424%	1.1264%
Arabinose	0.0448%	0.9086%	0.0424%	1.0086%
Fructose	0.0448%	0.9156%	0.0432%	0.9924%
Glucose	0.0448%	0.8892%	0.0424%	0.9638%
Starch	0.0432%	1.1026%	0.0424%	1.1284%
Control	0.0416%	0.4208%	0.0416%	0.4208%

- (3) *Fixation with unsterile oxides.* In these experiments 50 grams of oxide were mixed with 1 gram glucose. Experiments were started on 25-2-1940 and analyzed on 28-4-1940

	(Light)			(Dark)		
	Total N	Total C	Total bacteria	Total N	Total C	Total bacteria
MnO ₂	.. 0.015%	0.3128%	1.96	0.0058%	0.4286%	2.92
CuO	.. 0.0088%	0.5092%	0.62	0.0027%	0.6498%	0.88
CoO	.. 0.0187%	0.3035%	1.02	0.0085%	0.4012%	3.20
Ni ₂ O ₃	.. 0.0235%	0.2968%	0.98	0.010%	0.3862%	2.98

Nitrogen fixed per gram of carbon oxidized

	Light		Dark	
MnO ₂	30.78 mgs.	15.61 mgs.
CuO	30.26 "	17.97 "
CoO	37.66 "	21.31 "
Ni ₂ O ₃	46.7 "	24.16 "

- (4) *Nitrogen fixation with oxides and carbonates of metals under sterile conditions (1 litre Pyrex flasks) in light on the addition of glucose*

In the following experiments 25 gms. of oxide were taken to which 0.5 gram glucose was added

Started on 13-2-1940 and analyzed on 1-9-1940

	(Light)		
	Total N	Total C	N fixed per gram of carbon oxidized
ZnO	0.0048% 0.4826% 15.12 mgs.
Al ₂ O ₃	0.0038% 0.5348% 14.33 "
Fe ₂ O ₃	0.0056% 0.5016% 18.76 "
Ni ₂ O ₃	0.0056% 0.4972% 18.49 "
CoO	0.0048% 0.5124% 16.66 "
CuO	0.0020% 0.6628% 14.43 "
MnO ₂	0.0048% 0.4624% 14.21 "
CuCO ₃	nil 0.7084% ..
MnCO ₃	nil 0.6928% ..
CoCO ₃	nil 0.7084% ..

Analyzed on 1-9-1940

(Dark)		
ZnO
Al ₂ O ₃
Fe ₂ O ₃
Ni ₂ O ₃
CoO
CuO
MnO ₂
	0.0017%	0.5892% 8.06 mgs.
	0.0017%	0.6084% 8.87 "
	0.0020%	0.6172% 10.94 "
	0.0020%	0.6108% 10.57 "
	0.0020%	0.6084% 10.43 "
	nil	0.7124% nil
	0.0017%	0.6084% 8.87 "

The following experiments were conducted under completely sterile conditions in pyrex glass vessels

25 gms. oxide + 0.5 gm. glucose + 0.5 gm. V_2O_5 were exposed without any combined nitrogen to start with. Experiments started on 18-7-40. The light set was analyzed on 2-12-40 and the dark set on 28-1-1941

Experiment	(Light)			(Dark)		
	Total N	Total C	Nitrogen fixed per gram of C oxidized	Total N	Total C	Nitrogen fixed per gram of C oxidized
$ZnO + V_2O_5$	0.0056%	0.4628%	16.6	0.002%	0.5762%	8.47
$Fe_2O_3 + V_2O_5$	0.0056%	0.4934%	18.5	0.002%	0.5884%	9.40
$Al_2O_3 + V_2O_5$	0.0048%	0.5086%	16.4	0.0017%	0.5912%	8.1
$MnO_2 + V_2O_5$	0.0048%	0.4702%	14.8	0.0017%	0.6004%	8.5
$Ni_2O_3 + V_2O_5$	0.0056%	0.4826%	17.6	0.002%	0.5884%	9.4

It is highly interesting to note that the nitrogen fixed per gram of carbon oxidized under completely sterile conditions in soils in quartz flasks is 12.2 mgs. in light and 4.5 mgs. in the dark.

Similarly, from the experiments carried on in Pyrex glass, which cuts off more light, especially the ultra-violet, than quartz, the mean nitrogen fixation is 10.74 mgs. per gram of carbon oxidized under perfectly sterile conditions in light, whilst in the dark the fixation is 4.5 mgs. The order of these fixations under sterile conditions is practically the same as obtained without sterilization in soils.

It appears, therefore, that the efficiency of nitrogen fixation, whether the soil contains *Azotobacter* or is sterile, is practically the same. In other words, the means by which the energy material is oxidized and the energy is made available does not affect the efficiency of the process.

When the energy materials are added to the soil, they are oxidized with the liberation of energy, and this energy is utilized in nitrogen fixation under ordinary conditions. In natural conditions the energy materials are oxidized on the soil surface and also oxidized by the living organisms. But under sterile conditions, the micro-organisms are destroyed and the phenomenon of oxidation is a non-biological surface reaction. But the efficiency of the two processes, as far as nitrogen fixation is concerned, is of the same order in soils. Hence we are forced to conclude that nitrogen fixation can take place in as efficient a manner as possible in soils as well as

in surfaces in the same way as in natural conditions in the presence of living organisms.

With the carbonates of copper, manganese and cobalt no nitrogen fixation was observed, possibly due to their slight decomposition forming carbon dioxide which might have displaced the oxygen necessary for nitrogen fixation.

From the foregoing results it is clear that the amount of nitrogen fixation per gram of carbon oxidized with surfaces like ZnO , Al_2O_3 , Fe_2O_3 , Ni_2O_3 , CoO , MnO_2 , etc., with glucose as energy material is much greater than with soil under comparative conditions, both in light and in the dark as well as in sterile and unsterile conditions. These results showing that nitrogen fixation is possible with pure surfaces both in light and in the dark and that the efficiency of this process is greater with oxides than in soil are of fundamental importance. For nitrogen fixation neither soils nor bacteria are absolutely necessary, what really seems indispensable is a suitable surface where oxygen, nitrogen and an energy material are properly adsorbed and are in intimate contact. The energy material in contact with oxygen is oxidized on the surface and liberates energy necessary for the combination of nitrogen and oxygen. When light acts on the system a part of it is absorbed and causes a greater fixation of nitrogen. Hence in all cases the fixation of nitrogen is greater in light than in the dark.

We have emphasized that the nitrogen fixed in the form of protein and amino acid does not remain in the combined state for a long time because the combined nitrogen has a tendency to undergo oxidation in air specially in light first into ammonia then into nitrite and finally into nitrate. In this process there is always the possibility of the formation and decomposition of the unstable substance ammonium nitrite. In the soil there is already 0.05% nitrogen, hence in soil this type of loss of nitrogen is likely to be more pronounced than in the case of the oxides which are completely free from nitrogen to start with. Hence with oxides the loss of nitrogen being less than in soil the efficiency of the process appears to be greater in oxides than in soil using the same energy materials under comparable conditions. Moreover, with soils there is greater

chance of the formation of a compact mass specially on sterilization and hence the chances of aeration are less in soil than in the oxides. It is well known that aeration plays an important part in nitrogen fixation.

Probable mechanism of nitrogen fixation

It is believed that under both anaerobic and aerobic conditions, ammonia is the first product of nitrogen fixation, as ammonia is easily detected in the fixation of atmospheric nitrogen. Glucose has been found to decompose into pyruvic acid and hydrogen under anaerobic conditions according to the equation: $C_6H_{12}O_6 = 2CH_3COCOOH + 2H_2 + 12 \text{ Cal.}$ In the presence of the nitrogen of the atmosphere and on the soil surface, the hydrogen obtained from the decomposition of glucose may form ammonia according to the equation: $N_2 + 3H_2 = 2NH_3 + 24 \text{ Cal.}$

In the presence of oxygen, however, that is, under aerobic conditions, it is difficult to assume that ammonia is also the first product of nitrogen fixation. Because, in the presence of oxygen, glucose can undergo one or more of the following oxidations on the soil surface:—

- (1) $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 676 \text{ Cal.}$
- (2) $C_6H_{12}O_6 + 4\frac{1}{2}O_2 = 3C_2H_2O_4 + 3H_2O + 493 \text{ Cal.}$
Oxalic acid.
- (3) $C_6H_{12}O_6 + 1\frac{1}{2}O_2 = C_6H_8O_7 + 2H_2O + 199 \text{ Cal.}$
Citric acid.
- (4) $C_6H_{12}O_6 + O_2 = C_6H_{10}O_7 + H_2O + x \text{ cal.}$
Glycuronic acid.
- (5) $C_6H_{12}O_6 + \frac{1}{2}O_2 = C_6H_{12}O_7 + x \text{ cal.}$
Gluconic acid.

It seems that in the presence of air, the first change (1) is the most important. The above organic acids, which may be produced under aerobic conditions in small quantities and the organic acids (e.g. acetic, propionic, butyric, lactic, etc.), and traces of alcohol, glycerol, etc., which may be generated under anaerobic conditions are also easily oxidized to carbonic acid on the soil surface liberating energy. Hence, a large quantity of energy is available on the soil surface

for nitrogen fixation on the addition of molasses or other energy materials.

In the soil containing compounds of iron, manganese, traces of titanium, copper, etc., which are excellent catalysts in oxidation reactions and exposed to sunlight and air, the oxidation of the energy materials is certainly due to bacteria, light and chemical catalysts all acting simultaneously. For obtaining the hydrogen required for ammonia formation, the following reaction has to take place: $\text{H}_2\text{O} = \text{H} + \text{OH} - 112 \text{ Cal.}$ The direct combination of nitrogen and oxygen forming nitric oxide according to the equation: $\text{N}_2 + \text{O}_2 = 2\text{NO} - 43.2 \text{ Cal.}$ appears to require less energy than the process leading to the formation of ammonia. It appears, that the iron compounds, traces of manganese and copper compounds and sunlight, which falls on the soil surface, can facilitate the formation of nitric oxide from oxygen and nitrogen of the air. The nitric oxide can be readily oxidized to nitrous and nitric acids, which form nitrates in the soil.

Dhar and Mukherjee¹⁰ have shown that solutions of nitrates and carbohydrates in the presence of sunlight and titanium oxide can readily form small amounts of amino acids, with copious production of ammonium salts. It is interesting to note that ammonium salts and carbohydrates when exposed to sunlight in the presence of titanium oxide do not, however, form amino acids. It is well known that in plants the proteins, which are mostly the condensation products of amino acids, are only formed when carbohydrates have already accumulated by photosynthesis. The carbohydrates formed by photosynthesis in plants react with nitrates absorbed by plants from the soil and this results in the production of amino acids, proteins and ammonium salts in the plants. As a matter of fact, Waynick and Woodhouse (California. Agric. Station Annual Report, 1918-1919, pp. 62-63) have obtained evidence of amino-acid formation in nitrogen fixation by *Azotobacter*. It is believed that in the first few days of the growth of *Azotobacter* amino acids accumulate and later on proteins increase. In our experiments with pure cultures of *Azotobacter* thriving in mannite we have been able to detect amino acids by the valuable 'ninhydrin' test in the filtered liquids obtained by crushing

the *Azotobacter* cells with sand in a pestle and mortar. According to Jodidi¹¹, Schreiner and Skinner¹² and Lathrop¹³ several amino acids are of common occurrence in the soil. These amino acids may be obtained either by the hydrolysis of proteins added to the soil as manure or formed synthetically as explained above. It seems likely, therefore, *in vitro* as well as in the plant and in the soil, the nitrate is reduced to ammonia by the action of carbohydrates or other carbonaceous compounds with simultaneous formation of amino acids in small quantities. Hence, it appears that nitrates are first produced in nitrogen fixation and the nitrates react with the energy-rich materials present in the soil with the formation of ammonium salts and small amounts of amino acid.

It has already been stated that the efficiency of nitrogen fixation ($N_2 + O_2 + 43.2 \text{ Cal.} = 2NO$) in the electric arc process is low and only 1-2% of the electric energy is actually utilized. Similarly, the efficiency of nitrogen fixation by the absorption of chemical energy as explained in the foregoing pages is low; not more than one per cent of the chemical energy obtained from the oxidation of the energy materials is actually used up in this process. Also photosynthesis in plants ($6CO_2 + 6H_2O + 676 \text{ cal.} = C_6H_{12}O_6 + 6O_2$) is an inefficient process, not more than five per cent of the light energy is utilized in the formation of energy materials like carbohydrates, celluloses, etc.

NITROGEN FIXATION WITH CELLULOSIC MATERIALS— LEAVES, COWDUNG, ETC.

The following lines from Waksman¹⁴ show that the problem of the fixation of nitrogen in fields supplied with cellulosic materials has not yet been satisfactorily investigated.

‘The importance of this process in increasing the supply of soil nitrogen is, however, still questionable.’ (Page 448.)

‘It has been found that polysaccharids like celluloses can also serve as valuable sources of energy if they are first partially broken down by cellulose-decomposing organisms. However, these results need still further confirmation.’ (Pages 561-62.)

'Certainly the field results of A. Koch do not speak of any nitrogen fixation in the soil, following the addition of the celluloses and even straw.' (Page 588.)

1 kilogram soil + 20 grams Filter paper
(Exposed)

Date	NH ₃ -N	NO ₃ -N	Total nitrogen	Total carbon	Moisture	Azotobacter per gram of dry soil in millions
	%	%	%	%	%	
30-10-1936 (original soil) ..	0.0011	0.0020	0.0540	0.567	2.2	2.4
22-12-1936 ..	0.0008	0.0018	0.0540	..	3.8	3.7
20-1-1937 ..	0.0007	0.0016	0.0560	..	3.1	7.7
20-3-1937 ..	0.0006	0.0014	0.0583	..	3.0	12.5
7-5-1937 ..	0.0006	0.0012	0.0646	..	3.5	20.5
7-6-1937 ..	0.0006	0.0011	0.0677	..	3.1	27.2
8-7-1937 ..	0.0007	0.0014	0.0666	0.7012	..	18.0
13-9-1937 ..	0.0014	0.0021	0.0646	0.6704	..	12.0

Nitrogen fixed per gram of carbon oxidized = 18.1 mgm. (calculated).

1 kilogram soil + 20 grams Filter paper
(Dark)

30-10-1936 (original soil) ..	0.0011	0.0020	0.0540	0.5670	2.2	2.4
22-12-1936 ..	0.0007	0.0015	0.0540	..	4.8	4.3
20-1-1937 ..	0.0006	0.0012	0.0540	..	4.2	5.7
20-3-1937 ..	0.0006	0.0010	0.0552	..	4.0	25.5
7-5-1937 ..	0.0006	0.0009	0.0567	..	3.0	60.0
7-6-1937 ..	0.0006	0.0009	0.0575	80.0
8-7-1937 ..	0.0006	0.0009	0.0583	92.5
13-9-1937 ..	0.0008	0.0001	0.0608	0.6486	..	145.0

Nitrogen fixed per gram of carbon oxidized = 9.2 mgm. (calculated).

Plot 4 ft. by 4 ft. containing 20 kilograms cowdung
(Exposed)

Date	Total nitrogen	Total carbon	Moisture	Azotobacter per gram of dry soil in millions	Total bacteria per gram of dry soil in millions	Fungi per gram of dry soil
	%	%	%			
10-2-1937 (original soil) ..	0.0323	0.3294	1.7	1.05	10.7	22,000
12-2-1937 ..	0.0356	0.7126
7-3-1937 ..	0.0368	0.6384	3.0	6.5	20.5	32,000
5-4-1937 ..	0.0388	0.5616	3.5	15.5	65.5	41,000
29-4-1937 ..	0.0424	0.4826	3.0	32.0	160.0	30,000
25-5-1937 ..	0.0442	0.4108	3.0	30.0	170.0	28,000
12-6-1937 ..	0.0466	0.3825	3.5	28.5	165.5	28,000
28-9-1937 ..	0.0446	0.3789	3.2	15.8	115.2	25,000

Nitrogen fixed per gram of carbon oxidized = 33.3 mgm.

Plot 4 ft. by 4 ft. containing 20 kilograms cowdung

(Covered)

Date	Total nitrogen	Total carbon	Moisture	Azoto- bacter per gram of dry soil in millions	Total bacteria per gram of dry soil in millions	Fungi per gram of dry soil
	%	%	%			
10-2-1937 (original soil) ..	0.0356	0.3987	1.8	1.15	11.2	23,000
12-2-1937 ..	0.0381	0.7218
7-3-1937 ..	0.0385	0.6586	4.0	7.5	26.5	40,000
5-4-1937 ..	0.0392	0.5944	4.0	21.5	112.0	56,000
29-4-1937 ..	0.0403	0.5168	3.5	48.5	270.0	59,000
25-5-1937 ..	0.0411	0.4684	4.0	55.0	315.0	48,000
12-6-1937 ..	0.0420	0.4158	4.5	65.5	335.0	46,000
28-9-1937 ..	0.0428	0.4012	5.0	49.5	300.0	41,000

Nitrogen fixed per gram of carbon oxidized = 14.6 mgm.

The foregoing results show that the cellulosic substances like filter paper, dry leaf, etc., when mixed with soil and exposed to sunlight or kept in the dark or diffused light cause nitrogen fixation. When mixed with small amounts of molasses the cellulosic substances undergo oxidation more readily and cause greater fixation of atmospheric nitrogen. The nitrogen fixation in sunlight is greater than in the diffused light or in the dark. Similar results have been obtained with cowdung. These results are most important, because they show that cellulosic materials, plant residues, leaves, cowdung, etc., not only increase the humus content of the soil, and improve the soil tilth, moisture retention capacity but also act in the conservation of the soil by nitrogen fixation. Hence cowdung, which is used as a manure, has been found to supply to the soil not only the nitrogen it contains but it can also add nitrogen to the soil from the nitrogen of the air by fixation. In all our experiments the carbon has been found to decrease with time due to its oxidation. With cowdung the carbon-nitrogen ratio attains the normal value in field trials within two months after its application.

According to Mutterlein's calculation (Mutterlein, 1913) one acre of soil in Germany receives yearly about 200 kgms. of cellulose in the form of manure. It appears that this large amount of cellulosic

matter added to the soil may be partially utilized in nitrogen fixation in temperate climates. In tropical climates, due to the high temperature and great intensity of sunlight and the greater activity of the *Azotobacter*, the soluble carbohydrates, pentosans and cellulosic substances are oxidized at the soil surface at a great speed with the liberation of large amounts of energy necessary for nitrogen fixation. Hence manuring of tropical soils by the application of molasses and cellulosic materials is a highly important practical proposition. We are of the opinion that Indian soils would have been exhausted from the nitrogen point of view long ago had not the compensating agency, e.g. the fixation of atmospheric nitrogen by the addition of carbohydrates, pentosans and cellulosic materials to the soil, been counteracting the nitrogen loss. Moreover, the researches of Dhar and Atma Ram (1933) show that the tropical soil receives more available nitrogen from rain water than in temperate climates.

Russell ¹⁵ has reported that the nitrogen content of a grass land increased from 0.152% in 1856 to 0.338% in 1912. Similarly, a land permanently covered with vegetation for 24 years showed an increase from 0.108% to 0.145%. It appears that this increase in the total nitrogen content of these soils is chiefly due to the fixation of nitrogen from air caused by the liberation of energy from the oxidation of cellulosic and other carbonaceous substances on the surface of the soil.

After the harvest a part of the crop, namely the roots together with a portion of the stem, is left behind in the field. These are ploughed into the soil whereby they undergo oxidation liberating energy which causes the fixation of atmospheric nitrogen. Therefore, the nitrogen fixation due to the cellulosic substances, pentosans and carbohydrates present in the plant residues that are left behind after the harvest clearly explains why the Indian soils are not becoming exhausted. In cold countries, chiefly due to the inactivity of *Azotobacter* caused by the low temperature of the soil and lack of sunlight, the cellulosic and other energy materials added to the soil along with plant residues are not oxidized as readily as in tropical soils and hence large amounts of nitrogen fixation is not possible

in the soils of temperate countries. This explains the slow deterioration of the unmanured fields of Rothamsted as shown below.

Dr. J. A. Voelcker¹⁶ recorded the following results at Rothamsted in the case of wheat grown on fields continuously unmanured for over forty years.

			Crop yield in bushels per acre.
8 years (1844-51)	17
20 years (1852-71)	13.9
20 years (1872-91)	11.1

In tropical countries almost a constant yield of crop is possible due to the fixation of atmospheric nitrogen by the oxidation of the energy materials contained in the plant residue left in the soil.

Schroder computes that roughly 35 billion kilograms of cellulose are added to the Earth every year. From our experiments on nitrogen fixation with cellulosic materials we find that about 18 mgs. of nitrogen are fixed per gram of carbon oxidized from filter paper in light and about 9 mgs. in dark. While with cowdung the corresponding results are respectively 33 mgs. and 14 mgs. light and dark.

Hence, from the 35 billion kgms. of cellulose added to the soil, on a moderate estimate of 10 mgs. of average nitrogen fixation per gram of carbon oxidized, about 13,000,000 metric tons of nitrogen are added to the Earth by fixation (cf. the total output of N fixed synthetically in the world is 3,547,352 tons).

From our experiments we can conclude that out of the total 13,000,000 metric tons at least 50%, i.e. 6,500,000 metric tons of nitrogen are fixed in soils by the absorption of solar light. It appears, therefore, that much more nitrogen is fixed in nature by light absorption than that fixed by the industrial processes. Hence, in the economy of nature, next to photosynthesis in plants, the influence of light on nitrogen fixation leads to incalculable benefit to humanity and is of very considerable value.

Fat as energy material in nitrogen fixation

We have used both butter and ghee (clarified butter) as energy materials in nitrogen fixation. We have observed that the oxidation of these substances when mixed with soil is slower than the oxidation of carbohydrates and even that of cellulosic materials.

The following results have been obtained in dishes, as well as in fields:—

1 kilogram soil + 20 grams butter

(Exposed)

Date	NH ₃ -N	NO ₃ -N	Total nitrogen	Total carbon	Moisture	Azotobacter per gram of dry soil in millions
	%	%	%	%	%	
13-10-1936 (original soil) ..	0.0014	0.0032	0.0570	0.6156	1.8	5.1
14-11-1936	0.0015	0.0032	0.0570	1.4195	2.6	5.8
15-12-1936	0.0016	0.0032	0.0570	1.3883	3.1	7.6
13-1-1937	0.0014	0.0029	0.0570	1.3497	3.5	9.5
18-2-1937	0.0009	0.0024	0.0591	1.1968	3.0	12.0
11-5-1937	0.0007	0.0011	0.0617	0.9381	3.0	35.0
11-9-1937	0.0006	0.0010	0.0646	0.6654	3.0	25.0
12-10-1937	0.0009	0.0011	0.0626	0.6318	3.2	15.6

Nitrogen fixed per gram of carbon oxidized = 10.07 mgm.

1 kilogram soil + 20 grams butter

(Dark)

Date	NH ₃ -N	NO ₃ -N	Total nitrogen	Total carbon	Moisture	Azotobacter per gram of dry soil in millions
	%	%	%	%	%	
13-10-1936 (original soil) ..	0.0014	0.0032	0.0570	0.6156	1.8	5.1
14-11-1936	0.0014	0.0032	0.0570	1.4564	3.9	6.6
15-12-1937	0.0015	0.0030	0.0570	1.4278	4.0	8.5
13-1-1937	0.0002	0.0028	0.0570	1.3962	4.4	14.6
18-2-1937	0.0007	0.0021	0.0583	1.2854	4.0	20.0
11-5-1937	0.0006	0.0010	0.0591	1.0952	4.0	50.0
11-9-1937	0.0006	0.0009	0.0600	0.7456	3.5	70.0
12-10-1937	0.0007	0.0009	0.0591	0.6036	3.8	58.8

Nitrogen fixed per gram of carbon oxidized = 4.22 mgm.

Plot 4 ft. by 4 ft. containing 2 kilograms of Ghee

(Exposed)

Date	T.N.	T.C.	Moisture	Azotobac- ter per gram of dry soil in millions	Total bac- teria per gram of dry soil in millions	Fungi per gram of soil
	%	%	%			
26-1-1937 (original soil) ..	0.0368	0.3901	1.56	1.35	14.5	29,000
28-1-1937 ..	0.0368	1.0797
6-4-1937 ..	0.0381	0.9876	2.5	7.5	32.5	38,000
4-5-1937 ..	0.0392	0.8873	3.0	20.0	95.5	36,000
26-5-1937 ..	0.0400	0.8136	3.5	46.5	160.5	30,000
14-6-1937 ..	0.0407	0.7194	..	40.0	196.0	33,000
22-9-1937 ..	0.0439	0.4528	3.3	38.4	205.8	28,000
27-10-1937 ..	0.0420	0.4318	4.8	20.6	175.6	27,000

Nitrogen fixed per gram of carbon oxidized = 11.0 mgm.

Plot 4 ft. by 4 ft. containing 2 kilograms of Ghee

(Covered)

Date	T.N.	T.C.	Moisture	Azotobac- ter per gram of dry soil in millions	Total bac- teria per gram of dry soil in millions	Fungi per gram of soil
	%	%	%			
26-1-1937 (original soil) ..	0.0381	0.4115	1.6	1.4	13.6	28,000
28-1-1937 ..	0.0381	1.0941
6-4-1937 ..	0.0381	1.0313	3.0	8.5	64.0	45,000
4-5-1937 ..	0.0388	0.9487	4.0	32.5	175.0	48,000
26-5-1937 ..	0.0392	0.8906	4.0	66.0	245.0	46,000
14-6-1937 ..	0.0400	0.8205	3.0	85.0	295.0	42,000
22-9-1937 ..	0.0411	0.5316	5.0	94.0	330.0	40,000
27-10-1937 ..	0.0411	0.4424	5.0	68.5	290.0	35,000

Nitrogen fixed per gram of carbon oxidized = 4.6 mgm.

The experimental results show clearly that both butter and ghee are slowly oxidized and cause nitrogen fixation, which is practically the same as with that of carbohydrates and cellulosic materials. Moreover, the nitrogen fixation in sunlight is nearly double that in the dark although numbers of *Azotobacter*, total bacteria and fungi are much less in light than in the dark. The moisture content of the soil shows that it is fairly dry. It has been reported as follows by Waksman¹⁷: 'Fats decompose only slowly in moist soils, and almost not at all in dry soils'. According to Rubner¹⁸ only 22.9% of butter fat added to soil was decomposed during a period of one year and 32.8% in 12 years.

We have carried on experiments with pure glycerol both in dishes and in fields and we have observed that when glycerol is mixed with soil it leads to nitrogen fixation in the same way as carbohydrates. We have also observed that glycerol when added to soil and exposed to light is readily converted to reducing sugars.

From our experimental observations it is quite clear that along with carbohydrates, celluloses and even fats which are constituents of plant residue when added to soil are slowly oxidized and cause nitrogen fixation.

NITROGEN FIXATION IN SOILS CONTAINING NITROGENOUS COMPOUNDS

It is generally believed that the bacterial nitrogen fixation is inhibited when nitrates, ammonium sulphate, etc., are already present in the soil. This view has been emphasized by Waksman¹⁹: 'Nitrates are readily utilized by *Azotobacter* as sources of nitrogen; accordingly, the presence of nitrates in the medium inhibits the fixation of atmospheric nitrogen. Ammonium sulphate and peptone are also available nitrogen compounds. One-half milligram of nitrogen in an available form is sufficient to inhibit completely the fixation process.'

Recently, Fuller and Rettger²⁰ have reported that in the presence of ammonium sulphate and potassium nitrate nitrogen fixation was considerably retarded by several strains of *Azotobacter chroococcum* in culture media but several nitrogenous compounds did not affect materially the nitrogen fixation. These authors have concluded in agreement with Bonazzi²¹ and others that *Azotobacter* utilizes available combined nitrogen where possible instead of following the more laborious process in fixing free nitrogen.

We have carried on systematic work on the fixation of atmospheric nitrogen in fields or dishes supplied with nitrogenous compounds like oilcakes, urea, gelatine, blood, etc., with and without molasses. Our observations show that there is appreciable nitrogen fixation both in plots and dishes containing different nitrogenous substances and molasses.

The following results have been obtained with oilcakes, containing 5.71 to 6.03% of nitrogen:—

NITROGEN FIXATION WITH OILCAKES

Experiments in fields

10 tons of oilcakes with or without 2 tons molasses per acre of land

		Originally present on 18-9-1936 %	Analyzed on 9-10-1936 %	Analyzed on 14-11-1936 %	Analyzed on 24-12-1936 %
Mustard oilcake ..	C	= 0.6376	C = 0.43920	C = 0.41400	C = 0.4067
	N	= 0.1520	N = 0.13590	N = 0.11870	N = 0.1102
	C: N	= 4.19	NO ₃ = 0.00700	NO ₃ = 0.01836	NO ₃ = 0.02058
			NH ₃ = 0.00482	NH ₃ = 0.00222	NH ₃ = 0.0195
			C: N = 3.23	C: N = 3.23	C: N = 3.68
Mustard oilcake Molasses.	C	= 0.7504	C = 0.67680	C = 0.55080	C = 0.36000
	N	= 0.1485	N = 0.1505	N = 0.15730	N = 0.16470
	C: N	= 5.05	NO ₃ = 0.00823	NO ₃ = 0.01571	NO ₃ = 0.02333
			NH ₃ = 0.00848	NH ₃ = 0.00325	NH ₃ = 0.0225
			C: N = 4.9	C: N = 3.51	C: N = 2.18
Neem oilcake ..	C	= 0.7025	C = 0.6000	C = 0.72960	C = 0.4560
	N	= 0.18133	N = 0.1707	N = 0.1573	N = 0.1060
	C: N	= 3.874	NH ₃ = 0.00373	NH ₃ = 0.01555	NH ₃ = 0.00254
			NO ₃ = 0.00636	NO ₃ = 0.01077	NO ₃ = 0.02333
			C: N = 4.1	C: N = 4.63	C: N = 4.3
Neem oilcake Molasses.	C	= 1.0763	C = 0.82560	C = 0.8160	C = 0.7560
	N	= 0.1826	N = 0.24560	N = 0.2641	N = 0.18660
	C: N	= 5.89	NO ₃ = 0.00528	NO ₃ = 0.01037	NO ₃ = 0.03180
			NH ₃ = 0.01031	NH ₃ = 0.00304	NH ₃ = 0.00239
			C: N = 3.36	C: N = 3.1	C: N = 4.05

Experiments in dishes with alkali soils (pH 10.8)

				Analyzed on 13-11-1936 %	Analyzed on 14-12-1936 %
Mustard oilcake	..	50 grms.	Exposed to light	C = 3.2400	C = 2.0160
Soil	..	500 grms.		N = 0.3862	N = 0.3111
				NH ₃ = 0.00800	NH ₃ = 0.0053
				NO ₃ = 0.01400	NO ₃ = 0.0133
				C: N = 8.39	C: N = 6.67
Mustard oilcake	..	50 grms.	Exposed to light	C = 5.0160	C = 2.1120
Soil	..	500 grms.		N = 0.2800	N = 0.4000
				NH ₃ = 0.0063	NH ₃ = 0.00417
				NO ₃ = 0.0133	NO ₃ = 0.01555
				C: N = 14.32	C: N = 5.27
Molasses	..	50 grms.			

The foregoing results with oilcakes show that in the presence of molasses, there is appreciable nitrogen fixation with mustard and neem oilcakes, although in the absence of molasses these cakes lose nitrogen, apparently by aerobic denitrification. A very important result is brought about by these experiments in which it is observed that when the carbon-nitrogen ratio of the soil containing a mixture of oilcakes and molasses is even as low as 5.05, there is appreciable nitrogen fixation.

Similar results have been obtained in fields containing a mixture of ammonium sulphate and molasses. It has been observed that in several of these fields containing both ammonium sulphate and molasses there is nitrogen fixation.

With alkaline soils, fixation of nitrogen has been observed when the carbon-nitrogen ratio is less than 10. In view of these experimental observations proving the possibility of nitrogen fixation in soils, both normal and alkaline with low carbon-nitrogen ratio, the generally accepted significance of carbon-nitrogen ratio as stated by Russell²² in the following words has to undergo modification:—

The changes affecting the carbon and those affecting the nitrogen are intimately associated. The nitrogen can appear as nitrate only if it exceeds a certain critical amount relatively to the carbon, usually if the ratio C/N is 12 or less. When the proportion of carbon is greater, the excess goes off as CO₂ and the nitrogen remains as complex protein, any ammonia or nitrate present is also converted into protein, when, on the other hand, the proportion of nitrogen becomes greater, the excess is changed into nitrate. This intimate relationship arises from the fact that the decomposition of the organic matter is brought about by micro-organisms.

Our observations showing appreciable nitrogen fixation in soils containing 0.15% nitrogen or more cannot be explained from the bacterial view-point of nitrogen fixation and are in agreement with our view that nitrogen fixation in soils can take place not only under arid conditions where the total nitrogen content of the soil is low and is of the order of 0.05% but nitrogen fixation is also possible in soils of temperate countries where the total nitrogen

content of the soil is 0.1% or more, specially when there is sunshine and enough carbonaceous materials like molasses, leaves, etc., have been added and well mixed with soils. Workers in temperate countries should investigate this important manner of enriching soils.

Researches carried on for a number of years in the Allahabad University Chemical Laboratory have established that the nitrogen content of a soil is intimately connected with the carbon supply. The carbonaceous compound can fix the atmospheric nitrogen and thus increases the nitrogen content of the soil and also retards the loss of nitrogen in the form of nitrogen gas from the soil. From a very long time some workers have emphasized the importance of organic manures but the true function of carbonaceous substances in the soil has been discovered in the Allahabad University Chemical Laboratory.

Even as early as the middle of the last century, Liebig stated as follows regarding ancient Rome:—

‘The sewers of the immense metropolis of the ancient world engulfed in the course of centuries the property of the Roman peasants, and when the fields of the latter would no longer yield the means of feeding her populations, these same sewers devoured the wealth of Sicily, Sardinia, and the fertile lands on the coast of Africa.’

Describing medieval agriculture in England Prothero wrote:—

‘There was little to mitigate, either for man or beast, the horrors of winter scarcity. Nothing is more characteristic of the infancy of farming than the violence of its alterations. On land which was inadequately manured, and on which neither field turnips nor clovers were known till centuries later, there could be no middle course between the exhaustion of continuous cropping and the rest cure of barrenness.’

Due to the pioneering efforts of the late Prof. F. Haber large quantities of ammonium salts are manufactured in most countries but the problem of agriculture and of nitrogen conservation cannot be met specially in tropics by the provision of mineral compounds

on any scale brought about by rapid industrial developments, as the nitrogen added as ammonium salts is lost readily from soils.

In a review of work on organic manures by Dr. G. Ruschmann (1931) in Biedermann's Central-Blatt the following statement occurs:—

‘The Humus Question—The humus economy is not only for Germany but for all civilized European States with their extensive agriculture an ever burning question. The evils of one-sided measures for manuring assume continually more obvious forms. However much mineral manures serve to increase the yield for the moment, so much the less can they safely maintain their position. This knowledge is spreading both among scientists and practical men. In spite of constant or increasing use of mineral manures yields are decreasing.

The increase of soil fertility, which is the aim of all modern scientific and practical effort, cannot be attained by mineral manures. These by accelerating the breaking down of humus are actually detrimental. Increase of crop by improving the soil properties, and greater returns by addition of plant food are two different things, which are often confused. The latter can be effected by mineral manures which act immediately. On the other hand, to build up a good soil is a more lengthy process. While it is relatively simple to maintain the fertility of soil rich in humus, it is difficult in a soil which is mainly mineral to build up the necessary humus.

Arable soil is a living thing. The complaints of insufficient or completely negative results with mineral manures are rapidly increasing.

The humus capital of German soil has, according to Löhnis, a value of 30 milliards of Reichs-marks although Germany possesses mainly sandy soil. To increase this capital by skill is the important task of both the agricultural and business community. Humus capital puts every other kind of soil wealth on one side. Directly or indirectly all plant and animal life is made possible by the soil humus. To its increase may be systematically employed all those organic materials which at present are virtually wasted. The greatest attention should be devoted to the albuminous or nitrogen

containing organic rejecta and residues of human and animal life. We are to-day still far from the general knowledge of what great importance attaches to all organics and the energy contained in them which comes to us through the sun's rays, and which is set free by the decomposition of these substances in the soil.'

Nitrogen loss from soils and its retardation

Nitrogen being an elusive substance the nitrogen fixed or added as manure does not remain for a long time in the soil under ordinary circumstances.

The researches of Lipman and Blair²³, Russell and Richards²⁴, Shutt²⁵ and others show that nitrogen in the gaseous stage is lost from soils when the conditions are favourable for oxidation. The loss of nitrogen in this process may be more than double the amount of nitrogen taken up by the plant grown on the soil. Nearly 70% of the added nitrogen is said to have been lost when wheat plots in Rothamsted, England, have received annually 14 tons of farmyard manure containing 200 lb. nitrogen per acre.

A greater loss of nitrogen is observed when a manure is composted under aerobic than anaerobic conditions. According to Niklewski²⁶ there is more loss of nitrogen from stable manure in the presence of nitrifying bacteria than in their absence. It has also been reported that in the nitrification of different oil-cakes, the loss of nitrogen is the greatest with the most easily and quickly nitrifiable cakes. Recently, Viswanath²⁷ has obtained greater nitrogen loss and greater velocity of oxidation in the nitrification of ammonium salts than with farmyard or green manure. It is established that when there is a large amount of carbonaceous matter present in the manures along with the nitrogenous compounds, the velocity of the oxidation of nitrogenous compounds and the amount of nitrogen loss are decreased.

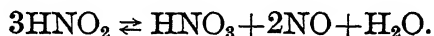
Experiments carried on at different places show that the total amount of nitrate present in soils containing crops is less than in neighbouring fallow soils even when a correction is applied for the amount of nitrate taken up by the crop. The oxidation processes are more vigorous in soils with crops than in those without them.

Russell ²⁸ has stated this problem of the loss of nitrogen in the following words: 'There is considerable difficulty in accounting for the nitrogen lost from the soil during the first 20 or 30 years of cultivation. It has, therefore, been supposed that nitrogen is evolved during the oxidation, and as all attempts to break off nitrogen from nitrate in these conditions have failed, it is assumed to come from the organic matter. This assumption involved the difficulty that no loss of nitrogen has been observed in the straightforward bacterial oxidation of organic substances such as albumin, asparagin or mixtures such as urine or faeces.' 'Yet somehow and somewhere gaseous nitrogen must be evolved to balance the considerable amount of fixation that is known to take place.'

The results obtained by Dhar, Tandon and Mukherji ²⁹ show that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark. The oxidation of ammonium salts by air is greater in light than in the dark and hence the possibility of the formation of ammonium nitrite is greater in light than in the dark. Several years ago, Dhar ³⁰ observed that solutions of ammonium nitrite decompose into nitrogen and water when exposed to sunlight and this photochemical decomposition is facilitated by acids and different solid surfaces. Moreover, the recent observations of Dhar, Tandon and Mukherji (*loc. cit.*) show that solutions of ammonium chloride and sodium nitrite decompose readily with the evolution of nitrogen when exposed to sunlight in glass beakers or quartz tubes mixed with sterilized or unsterile soil. This decomposition can take place under completely sterilized conditions in the complete absence of bacteria. Moreover, this decomposition is less pronounced in dilute solutions of ammonium nitrite and also when cane sugar is added to the solution containing ammonium and nitrite ions.

All these observations have been explained from the view-point that in the processes of ammonification and nitrification taking place in the soil or in solutions, ammonium nitrite is produced. Solutions of ammonium nitrite have been found to decompose into nitrogen and water readily by increase of temperature or exposing them to light. The formation of ammonium nitrite from ammonium

salts or proteins requires oxygen and that is why, this type of denitrification is facilitated by increased soil aeration and also soil acidity, as nitrous acid also undergoes decomposition according to the equation



This chemical change is also markedly accelerated by light.

There is also the possibility of the reaction of nitrous acid on amines, amides and amino acids, which may sometimes be formed in the decomposition of soil organic substances. This important phenomenon first studied systematically by Lipman and Blair and emphasized by Russell has now been satisfactorily explained by Dhar⁸¹ and collaborators. That this type of nitrogen loss from soils is chiefly due to the formation and decomposition of the unstable ammonium nitrite is supported by the fact that the soil loses nitrogen in this way much less when manured with sodium or potassium nitrate than when manured with ammonium sulphate or organic nitrogenous manures; because in the process of nitrification the unstable substance ammonium nitrite is formed. It has been postulated that this type of denitrification may be caused by the interaction of hyponitrous acid and hydroxylamine formed in nitrification. Unfortunately, the evidence in favour of the existence of these compounds in soil appears unsatisfactory.

Addition of carbonaceous substances like molasses tends to preserve the soil nitrogenous compounds present in the soil by decreasing the probability of the formation and decomposition of ammonium nitrite.

Retardation of nitrogen loss from soil with cowdung, green leaves, and molasses; 277.2 kg. of nitrogen as $(\text{NH}_4)_2\text{SO}_4$ per acre of land used.

Condition		NH ₃ nitrogen	NO ₃ nitrogen	Total nitrogen	Total carbon	Date of Analysis
		%	%	%	%	
Alone	..	0.028	0.0026	0.1167	0.3721	6-10-1936
Cowdung	..	0.035	0.003	0.1272	0.5046	„
Leaves	..	0.0304	0.0026	0.1137	0.3731	„
Molasses	..	0.028	0.0031	0.1272	2.435	„

Condition		NH ₃ nitrogen	NO ₃ nitrogen	Total nitrogen	Total carbon	Date of Analysis
		%	%	%	%	
Alone	..	0.0242	0.0039	0.100	0.3738	24-10-1936
Cowdung	..	0.0324	0.0036	0.1082	0.5044	"
Leaves	..	0.0236	0.0042	0.100	0.3792	"
Molasses	..	0.0296	0.0039	0.1167	2.421	"
Alone	..	0.0222	0.004	0.0875	0.3722	12-11-1936
Cowdung	..	0.0304	0.0039	0.100	0.5010	"
Leaves	..	0.0232	0.0049	0.0903	0.3812	"
Molasses	..	0.0294	0.0054	0.1158	2.301	"
Alone	..	0.0182	0.0061	0.0823	0.3768	26-11-1936
Cowdung	..	0.0196	0.0062	0.0934	0.498	"
Leaves	..	0.0194	0.0073	0.0908	0.431	"
Molasses	..	0.0248	0.006	0.1346	1.424	"
Alone	..	0.0017	0.0064	0.0583	0.3712	30-12-1936
Cowdung	..	0.0019	0.0078	0.0736	0.4882	"
Leaves	..	0.0017	0.0082	0.0712	0.5122	"
Molasses	..	0.004	0.0097	0.1273	0.9864	"

The above results show that the loss of nitrogen by the addition of ammonium sulphate to the field soil is also lessened by the addition of carbonaceous substances like cowdung, leaves, etc. With molasses and ammonium sulphate, there is nitrogen fixation.

FUNCTION OF ORGANIC MANURES

It will be clear, therefore, that the value of ammonium sulphate as a manure to be used specially in tropical countries should be greatly enhanced, if it is mixed with cowdung, leaves, molasses, fats or any other carbonaceous material. Oilcake containing fats and nitrogenous compounds has been found to be effective in tropical countries as nitrogenous manures, because fats are known to retard the oxidation and nitrification of the nitrogenous compounds in the soil. It is clear why farmyard or green manure produces better crop yield than ammonium sulphate alone, because, the carbonaceous substances present in the farmyard or green manure retard the nitrification of the nitrogenous compounds present in the soil and decrease the nitrogen loss. As a matter of fact, when farmyard manure is added to the soil more nitrogen is conserved

and fixed in the soil than with ammonium sulphate. This is evident from the following results obtained from the Rothamsted fields:—

	Total N %
1. Receiving no manure since 1843	0·095
2. Receiving farmyard manure since 1852	0·256
3. Receiving complete artificials + $(\text{NH}_4)_2\text{SO}_4$	0·099
4. Receiving complete artificials + farmyard manure	0·253
5. Receiving potash and phosphate but no nitrogen	0·090

Of course, too little oxidation of the protein present in the soil by the addition of molasses or other carbonaceous substances will not make the soil suitable for the growth of crops. It seems necessary that an equilibrium should be established between the oxidized and the unoxidized proteins, ammonium salts and other nitrogenous substances, which are present in the soil for maintaining its fertility at a proper level. Too much oxidation of the nitrogenous substances and ammonium salts may entail marked nitrogen loss by this type of denitrification and too little oxidation will not make the soil fertile enough for a good yield of crop. Hence the molasses or cellulosic materials or other carbonaceous substances should not be added in very large amounts and after the addition of molasses or other substances, the soil should be ploughed to help oxidation. Moreover, molasses and cellulosic materials (when added to soil and the soil is properly aerated for helping the oxidation reactions) cause nitrogen fixation by the increase of ammoniacal and total nitrogen contents of soil.

This type of nitrogen loss may amount to 100 lb. of nitrogen per acre annually, whilst the amount of nitrogen required by wheat (for example) per acre is 30–40 lb. Russell and his co-workers at Rothamsted have reported that during 47 years of application of manure to soil, 14% of the nitrogen was accumulated as humus, 25% had been utilized by the plants, and 60% was lost in the gaseous state, i.e. aerobic denitrification. Hence it is highly important to investigate this phenomenon and control this loss for increasing soil fertility.

The greater value of organic nitrogenous compounds or a mixture of ammonium salts and carbonaceous substances for the soil than ammonium salts lies in the fact that not only the soil texture is improved by the colloids added with the organic manure but the carbonaceous matter added acts as an agent in the preservation of the nitrogenous compounds of the soils by behaving as a negative catalyst.

Apart from this influence of the carbonaceous substances, sugars, cellulose, pentosans, fats, etc., on the conservation of soil nitrogen, these substances when added to the soil along with farm-yard or green manure, or straw, also leads to the fixation of atmospheric nitrogen in the soil. Hence the carbonaceous substances, like sugars, cowdung, cellulose, pentosans, fats, etc., added to the soil are not only effective in nitrogen conservation but cause nitrogen fixation as well. In a recent article Jenkins³² has discussed the use of organic manures but has not reported that organic manures help in the conservation and fixation of nitrogen in the soil. This aspect of the importance of organic manures in preference to artificials has been discovered by the present writers.

Our experimental results show that when 17·32 to 69·3 kgs. of nitrogen as ammonium sulphate are added per acre of soil along with molasses, there is appreciable nitrogen fixation in the soil even in the presence of ammonium sulphate, because the total nitrogen in fields to which molasses and ammonium sulphate have been added is always greater than at the beginning. These results cannot be explained from the bacterial view-point of nitrogen fixation, because it has been assumed that in presence of ammonium salt hardly any bacterial nitrogen fixation is possible. Hence our results showing an increase of nitrogen, when molasses is added to fields to which ammonium sulphate has already been added, support the view, that nitrogen fixation is partly bacterial and partly photochemical and catalytic.

From the summary of the results recorded above, it can be concluded that the value of the nitrogenous manure added depends considerably on the amount of the organic matter or humus present in arid soils. If the humus or organic matter content is low, the

nitrogen content is also low. The researches carried on in the Allahabad University Chemical Laboratory show that organic matter added to the soil not only improves the soil texture and increases the water retention capacity, but also leads to the increase in ammoniacal and total nitrogen due to the fixation of atmospheric nitrogen. The energy given out in the oxidation of the organic matter leads to the fixation of atmospheric nitrogen and this process requires energy. In the presence of sunlight or artificial light this fixation of nitrogen has been found to be increased. Hence under normal conditions in the soil with a good supply of organic matter nitrogen fixation actually takes place and that is why a good proportion of nitrogen actually exists in soils. In most tropical countries a steady crop yield is observed even without the addition of any artificial manures. This has been a puzzle to visitors from the West but the researches carried on at Allahabad have established that the cellulosic materials added to the soil as plant leaves, residue, etc., are oxidized in the soil and lead to nitrogen fixation in the soil itself aided by sunlight. This is the chief reason of the constant supply of nitrogen under tropical conditions.

Unfortunately, the nitrogen that is present in the soil or is fixed cannot remain in the soil for a long time as nitrogen is a very elusive substance and is readily lost as nitrogen gas and escapes into the atmosphere, when the soil conditions are favourable for oxidation. This phenomenon, frequently observed all over the world and reported by many workers, is due to the following fact. When any nitrogenous substances either organic compound or ammonium salts are added to the soil and the conditions are favourable for oxidation as in ploughing, the nitrogenous compounds undergo oxidation and form ammonia, nitrite and finally nitrate. As an intermediate state, there is always the possibility of the formation of ammonium nitrite in this process. It is well known that ammonium nitrite undergoes decomposition into nitrogen and water. This change is greatly facilitated by increase of temperature and by exposure to light or by soil acidity. Due to this process taking place in normal soils a great loss of nitrogen in the gaseous state has been observed all over the world when large quantities of

organic nitrogenous compounds or ammonium salts are added to the soil. This loss can be minimized by adding organic materials like carbohydrates, fats, etc., which retard the oxidation of the nitrogenous compounds.

Hence in order to save nitrogenous manures from marked loss due to the escape of gaseous nitrogen, organic matter (carbohydrates, fats, celluloses, etc.) must be present or added to the soil especially in arid regions and under tropical conditions. Carbohydrates and cellulose and fats have been found by us to prevent the loss of nitrogen from organic nitrogenous matter and ammonium sulphate and other ammonium salts. The value of organic matter, therefore, is to help the fixation of nitrogen and protection of the soil nitrogen by stopping the loss of nitrogen gas due to the formation and decomposition of the unstable substance ammonium nitrite. Both carbohydrates and fats are known to preserve proteins in the animal body. Similarly, these substances as well as the cellulose have been found by us to preserve soil nitrogen and hence in arid conditions organic matter should always be added to the soil to prevent the loss of nitrogen and thus a mixture of ammonium salts and organic matter has been generally found to be a better manure than ammonium salts alone. This point has been well brought out by experiments all over the world. Organic matter surely leads to nitrogen fixation from the air and nitrogen protection and that is why it is such a valuable commodity in the soil.

REFERENCES

- ¹ Nernst *et al.* Z. anorg. chem., 1905, 45, 126; 1906, 49, 213.
- ² Förster *et al.* Z. angew. chem., 1908, 21, 2161, 2209; 1910, 23, 2017.
- ³ Haber *et al.* Z. Elektrochem., 1907, 13, 725; 1908, 14, 689; 1910, 16, 11, 789, 796, 810.
- ⁴ Berthelot and Gaudechon. Compt. rend., 1910, 150, 1517.
- ⁵ Warburg *et al.* Ann. Physik, 1907 (4), 23, 209.

* Our experiments on nitrogen fixation have been corroborated by Dr. H. W. Kerr at Brisbane, by Dr. Shri Ranjan and Mr. Bhattacharya of the Botany Department, Allahabad University, by Mr. B. Ramamoorthy of the Imperial Institute of Agricultural Research, New Delhi, and by Mr. Sulaiman of the Dacca University, Dacca. It is stated that results obtained in Hawaii (Handbook of Hawaiian Soils, p. 190; also *International Sugar Journal*, 1937, 39, 419, 420) inexplicable under the biological hypothesis can be explained by the photochemical hypothesis of Dhar and co-workers.

- ⁶ Warburg. Z. Elektrochem., 1906, 12, 540.
- ⁷ Fischer and Hene. Ber., 1912, 45, 3652.
- ⁸ Grau and Russ. Sitzber. Akad. Wien, 1906, 115, 1.
- ⁹ Dhar and Mukherji. Proc. Nat. Acad. Sci. (India), 1935, 5, 61.
- ¹⁰ Dhar and Mukherji. J. Ind. Chem. Soc., 1934, 11, 727.
- ¹¹ Jodidi. J. Amer. Chem. Soc., 1910, 32, 396.
- ¹² Schreiner and Skinner. U.S. Dept. Agric. Bur. Soils Bulletin, 1912, 87.
- ¹³ Lathrop. J. Franklin Inst., 1917, 169, 183, 303, 465.
- ¹⁴ Waksman, S. A. 'Principles of Soil Microbiology', 1927.
- ¹⁵ Russell. 'Soil Conditions and Plant Growth', 1931, 362.
- ¹⁶ Voelcker, J. A. 'Improvement of Indian Agriculture', 1895, 37.
- ¹⁷ Waksman, S. A. 'Principles of Soil Microbiology', 1931, 404.
- ¹⁸ Rubner. Archiv. Hyg., 1922, 91, 290.
- ¹⁹ Waksman, S. A. 'Principles of Soil Microbiology', 1931, 505.
- ²⁰ Fuller and Rettger. Soil Science, 1931, 31, 219.
- ²¹ Bonazzi and others. J. Bact., 1921, 6, 33.
- ²² Russell. 'Soil Conditions and Plant Growth', 1932, 313.
- ²³ Lipman and Blair. Soil Science, 1921, 12, 1.
- ²⁴ Russell and Richards. J. Agric. Sci., 1917, 8, 495.
- ²⁵ Shutt. J. Agric. Sci., 1910, 3, 335.
- ²⁶ Niklewski. Roc. z. Nauk. Roln., 1923, 9, 1.
- ²⁷ Viswanath. Sci. Reports Dept. Agriculture, Madras, 1930-1931.
- ²⁸ Russell. 'Soil Conditions and Plant Growth', 1932, 368, 369.
- ²⁹ Dhar, Tandon and Mukerji. J. Ind. Chem. Soc., 1935, 12, 67.
- ³⁰ Dhar. Proc. K. Akad. Wet. Amsterdam, 1920, 23, 308.
- ³¹ Dhar *et al.* Nature, 1934, 134, 572.
- ³² Jenkins. Imp. Bureau Soil Sci. Tech. Com. No. 33, 1935.

STUDY I OF DR. C. R. REDDY BY
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C. V. Reddy
20. 8. 1960.

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written

PHOTOSENSITIZATION BY SOLIDS

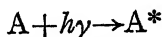
By

G. GOPALARAO

When matter and light interact there are many possibilities. When a light quantum ($h\nu$) interacts with a molecule, we may have—

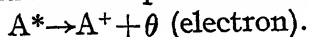
1. The Raman effect. In this, each mode of oscillation in the molecule which interacts with the light quantum results in an absorption of energy from this quantum, which will in consequence be scattered with less than its initial energy. If, however, a molecule in a vibrational or rotational level above the ground level interacts with the quantum of light, the energy of the scattered quantum may be higher. Thus Raman lines of higher frequency than the exciting radiation may be emitted.

2. The molecule or atom may absorb a quantum of radiation $h\nu$ (in the visible or ultraviolet) and pass from one electronic energy level into a higher one.



The fate of the excited particle A^* and the excess of energy associated with it depends on a variety of circumstances. The most important of the reactions which the excited particle A^* undergoes may be summarized as follows:—

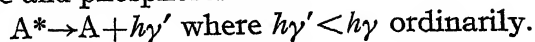
(a) External and internal photoelectric effect



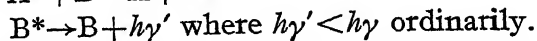
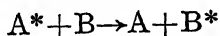
(b) Optical Resonance



(c) Fluorescence and phosphorescence



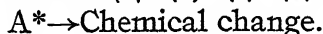
(d) Sensitized fluorescence



(e) The excess of energy of the excited particle may be dissipated into thermal energy by collisions of the second kind with other particles.

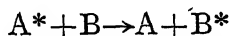
Sometimes several of the above equations may combine together.

(f) The excited particle may undergo chemical reaction instead of a physical one as pictured in (a), (b), (c), (d) and (e)



The most important types of chemical reactions which the excited particle may undergo are (1) Isomeric transformation, (2) Polymerization, (3) Dissociation, and (4) Reaction with other molecules.

(g) The excited particle may not itself undergo chemical change but may induce chemical change in other species of molecules in the neighbourhood



$B^* \rightarrow \text{Chemical change.}$

This phenomenon is called photosensitization or optical sensitization.

It is a general characteristic of photochemical sensitization processes, that in the reacting system there are two substances A and B, of which A takes up radiant energy without suffering any permanent chemical change, whilst B undergoes the true chemical change, though B is incapable of absorbing the active radiation. A is the absorbing component and B the reacting constituent. The substance A is called the photosensitizer.

Two cases of photosensitization may perhaps be differentiated:

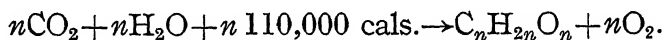
(a) in the absence of the photosensitizer no chemical reaction occurs when light is used within the frequency range which is effective when the photosensitizer is added to the system, (b) with light of a given frequency, reaction may take place partly as a sensitized and partly as a direct photochemical process.

Photosensitization has been first noticed by Vogel (1873) who showed that the photographic plate, which is ordinarily sensitive only to wavelengths less than 5300 \AA , may by the addition of certain dyes to the emulsion be made sensitive to radiation of greater wavelength which is absorbed by the dye. Since the discovery of Vogel many photosensitized reactions have been discovered and the numerous examples now available include (1) gas reactions sensitized by mercury vapour, chlorine, and bromine, and (2) reactions in liquid medium in which the absorbing constituents are the halogens,

iron salts, uranyl salts, various dyes, etc., (3) reactions in which a solid phase is involved, such as sensitization by zinc oxide, sensitization of the photographic plate by different dyes, and the natural process of carbon assimilation in the green leaves of plants where the pigment chlorophyll is the photosensitizer. Photosensitization of the third type involving a solid phase is of great theoretical and practical interest. It is proposed to discuss this at some length in the following pages.

The discovery of Vogel that a suitable dye absorbed on the silver bromide in the gelatin film makes the plate sensitive to red and infra-red light has laid the foundations of photography in the infra-red. At the present time, the manufacture of panchromatic plates is an industry of considerable importance. Among the dyes employed for sensitization may be mentioned (1) erythrosine, which sensitizes silver bromide to green light ($\lambda = 5500 \text{ \AA}$), pinacyanol for red ($\lambda = 6500 \text{ \AA}$), and rubrocyanine for infra-red ($\lambda = 8000 \text{ \AA}$).

The process of carbon assimilation by plants, on which animal life depends, is also one of photosensitization by a solid, namely the green pigment chlorophyll. The primary reaction in this process may be represented by the equation



Carbon dioxide is absorbed by the plant from the atmosphere and utilized in the synthesis of complex organic materials; this synthesis is an endothermic reaction and requires a supply of energy for its occurrence. This energy is derived from the sun's radiation. This photosynthetic reaction occurs in the visible part of the solar radiation, though carbon dioxide and water either severally or jointly do not have any absorption in this region. The effective radiation is absorbed by the green pigment chlorophyll which, however, does not undergo any final chemical change. The most important point to be noticed about photosynthesis is the very large accumulation of energy involved in the process. In fact, this is the only reaction known to Man and Nature, whereby the enormous floods of solar radiant energy are caught by the plant and converted into potential chemical energy in the shape of the food materials. It is this

stored up energy, which is released during the oxidation of the plant food materials in the animal body, that sustains animal life. Moreover, in a chemical sense our source of fuels and food is the same. It is now established that our present resources of coal and petroleum, the two sources of power for our modern industrial life, owe their origin to the fossil vegetation that has been buried under the bowels of the earth billions of years ago. The energy resident in the coal and petroleum is the solar radiant energy bottled up by the plants during vistas of time compared with which the total span of human history appears but a moment. The exploitation of coal and petroleum as sources of energy has produced a profound revolution in the fabric of human life in its social, economic and political aspects. But this civilization of coal and petroleum is wasteful, profligate; it is squandering away the principal of an enormous legacy of solar energy handed down by Nature at a rate much greater than that at which it is being replaced. There is every indication that at the present rate of consumption our reserves of coal and petroleum would not last us long. When they are exhausted shall we call a halt to our machine civilization on which we pride ourselves so much or are we to discover new modes of trapping and utilizing the solar radiant energy? The plant is the only known convertor of solar radiant energy into useful potential energy and the fundamental reaction is one of photosensitization by a solid. In spite of the great advances in Science, our knowledge of the mechanism of the photosynthetic reaction and the energy conversion involved therein is still obscure. Before we can invent a kind of 'super-plant' for the fixation of solar radiant energy we must unravel the mystery of photosynthesis. The key to this mystery lies in a clearer understanding of the mechanism of photosensitization by solids.

Photosensitization by solids is important in many other ways. A. Eibner¹ studied the photosensitized decolorization of various dyes in the presence of zinc oxide and light. The same author found that the paint material Prussian blue is reduced in light in the presence of glycerol and zinc oxide.

These results are of considerable interest in the fading of paints exposed to light. Moreover, it is now known that paints containing

titanium dioxide show fading and this phenomenon has been studied by Kiedel², Wagner³, and Brocker⁴. Tint paints containing titanium dioxide show bad fading regardless of whether the substance is introduced as titanium white, extended titanium-barium pigment or titanated lithophones. Similar effects have been observed in distempers and wall-papers loaded with titania and viscose fibres delustred with titanium white⁵. Several processes for improving the light resistance of titania paints have been described among which are treatment with chromium compounds⁶, tinting prior to calcination⁷, heating the titania with alkali⁸, or coating the particles with silicic acid⁹. Gopalarao and Dhar¹⁰ and Gopala Rao¹¹ have studied the photosensitized oxidation of ammonia in the presence of various photosensitizers, e.g. zinc oxide, titanium dioxide, aluminium trioxide, uranic oxide, silicon dioxide, etc. Gopalarao and Dhar¹² observed that the oxidative deamination of various amino acids in sunlight is markedly accelerated by these photosensitizers. Gopalarao and Pandalai¹³ studied the oxidation of different amines in aqueous solution when exposed to sunlight in the presence of photosensitizers mentioned above. Gopalarao and Varadanam¹⁴ have found that ferric oxide is a good photocatalyst for the oxidative deamination of amino acids in sunlight. Dhar and co-workers¹⁵ have brought forward considerable evidence to show that fixation of atmospheric nitrogen is favoured by sunlight and photocatalysts. The above workers have emphasized the significant importance of their results to soil chemistry.

The few instances cited above will show the importance of the phenomenon of photosensitization by solids. It is with a view to elucidate the mechanism of this phenomenon that work was undertaken in these laboratories for several years. In the course of our work we have discovered some new photosensitizers, such as stannic oxide, uranic oxide, ceric oxide, thorium dioxide, cadmium oxide, etc.

For the purpose of the elucidation of the mechanism of photosensitization by solids a simple reaction has been chosen, namely the oxidation of ammonia in aqueous solution, because such a simple reaction is susceptible of easy experimental control. When an

aqueous solution of ammonia is exposed to sunlight in a glass vessel no oxidation of ammonia occurs. But if the ammonia solution contains in suspension zinc oxide, titanium dioxide, uranic oxide, stannic oxide, ceric oxide, etc., oxidation of the ammonia to nitrite is noticed. But the oxides do not undergo any permanent chemical change. Thus the added oxides act as photosensitizers. When the ammonia solution is exposed in a quartz vessel to the ultraviolet light from a quartz mercury vapour lamp, there is a slow rate of oxidation of the ammonia. This rate is considerably increased by the addition of any one of the photosensitizers mentioned above. We have found that, of the photosensitizers so far studied by us, zinc oxide and titanium dioxide are the best.

Gopal Rao¹⁶ investigated the mechanism of photosensitized oxidation of ammonia using titanium dioxide. The main features of the reaction are—

(1) The oxidation of ammonia to nitrite in the presence of titania and sunlight occurs even if air be excluded.

(2) Increase in the amount of titania produces an increase in the reaction rate but this soon reaches a limiting value.

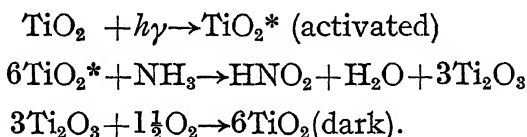
(3) The amount of nitrite formed increases proportionately to the time of exposure.

(4) The reaction velocity does not increase in proportion to the concentration of ammonia; a very large increase in the concentration of ammonia produces only a very slight increase in the reaction rate.

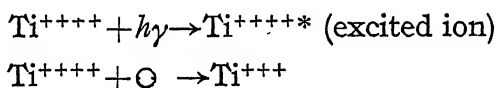
(5) The reaction is retarded by traces of salts of colorless cations like Na^+ , K^+ , NH_4^+ , Ba^{++} , Sr^{++} , Al^{+++} , etc. It has been found by us that divalent Ba^{++} and Sr^{++} ions are more effective retarders than monovalent Na^+ , K^+ and NH_4^+ ions and that trivalent Al^{+++} ions are more effective than the divalent ions.

(1) and (2) indicate that the photosensitizer takes a chemical part in the reaction. (3) and (4) indicate that the reaction is zero-molecular. This taken along with (5) shows that adsorption plays an important rôle in this reaction. Gopal Rao¹⁶ suggested that the reaction is a heterogeneous catalytic one occurring at the surface of titania. A molecule of titania on the surface gets activated due

to absorption of a quantum of radiation. The activated titania then oxidizes ammonia to nitrous acid, getting itself reduced to titanous oxide Ti_2O_3 or TiO . The titanous oxide then undergoes rapid oxidation by the dissolved oxygen, thus regenerating the photosensitizer. For this reaction to occur, there must be intimate association between the molecules of the photosensitizer and the ammonia and this is secured by adsorption



It may be that Ti^{++++} ion in a molecule of TiO_2 on the surface gets electronically excited on the absorption of a quantum of light. An electron is raised to a higher energy level and according to Franck and Haber¹⁷ such a molecule, atom or ion which possesses an unoccupied electronic level can take up an electron from a reducing substance which functions as an electron donor. Thus



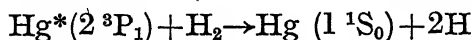
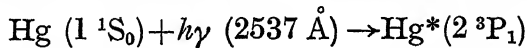
The photoactive particle takes up an electron and hence gets reduced. The reducing substance which donates the electron gets oxidized. It is well known that oxidation consists in loss of electrons and reduction in a gain of electrons.

It will be interesting to discuss the theory now proposed in relation to other theories of photosensitization proposed from time to time by various investigators.

The various theories proposed include the following:—

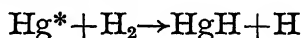
(1) The view that photosensitization is due to energy transfers by collisions of the second kind. This theory was suggested by Franck and Cario¹⁸ from their work on the sensitized dissociation of hydrogen and the sensitized fluorescence of thallium in the presence of mercury vapour. Cario and Franck were the first to note that when a mixture of mercury vapour and hydrogen is illuminated with the 2537 Å line, an active form of hydrogen is obtained. This

resembles atomic hydrogen in many of its properties. Cario and Franck, therefore, suggested the following mechanism:—



That such dissociation can occur is evident from the fact that the energy of excitation of Hg (2^3P_1) atom, namely 112,000 calories is greatly in excess of the minimum energy of 100,000 calories required for the dissociation of the hydrogen molecule. The mechanism postulated by Franck and Cario is, however, not the only one conceivable and two other possible mechanisms have been suggested.

Compton and Turner¹⁹ assumed the formation of a mercury hydride from spectrographic data



Dickinson²⁰, Mitchell²¹ and Rideal and Hirst²² assumed the formation of an excited hydrogen molecule with a high vibrational energy content.

Theoretical considerations suggest that all the above three modes of deactivation of the excited mercury atom may occur; However, Nordheim²³ considers that the most probable is the one involving the dissociation of the hydrogen molecule. The available experimental evidence cannot conclusively decide in favour of any one of the above.

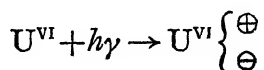
(2) The hypothesis that the primary action of light is to form a substance which enters into reaction with an acceptor, initiating a sequence of reactions which generates the sensitizer.

An example is the mechanism advanced by Winther for the sensitization of the Eder reaction by ferric salts. Here the absorption of light is presumed to activate the ferric ions which then react with oxalate and are themselves reduced to ferrous ions. The latter are then re-oxidized by mercuric chloride.

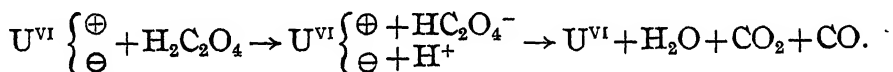
This is similar to the mechanism suggested by the author for the sensitization by titania; and this mechanism is doubtless applicable in many cases. Other examples are (1) the photodecomposition of ozone sensitized by chlorine and bromine, (2) the cis-trans transformation of maleic acid (or its esters) into fumaric acid

(or its esters) in visible light sensitized by bromine, (3) the bromine sensitized decomposition of the dibromide of phenylcinnamionitrile, and (4) the iodine sensitized oxidation of hydriodic acid solution. In all these cases there is evidence to show that the halogens take part by way of atoms.

(3) The theory of Baur that the elementary process in the action of light is the formation of a polarized molecule. If photochemical reaction subsequently ensues, this is regarded as a type of 'electrolysis' in which the 'anodic' and 'cathodic' constituents of the polar activated molecule react with the depolarizers present in the system. Applied to photosensitization by uranyl salts we have



The system thus formed has both oxidizing and reducing properties. Its action on oxalic acid can be represented according to Baur as follows:—



(4) The theory that sensitizers are fluorescent substances, which give rise to radiation of very short wavelength. This theory was suggested by Winther²⁴ from his experiments on the formation of ozone during the illumination of zinc oxide in the presence of oxygen, with light transmitted by glass ($\lambda > 3400 \text{ \AA}$). It is well known that in the absence of the photosensitizer this reaction occurs only in light of wavelength shorter than 2000 \AA . Direct physical tests for Winther's postulated emission by ZnO have so far yielded negative results; moreover, his postulate is in contradiction to Stoke's Law of fluorescence.

(5) The theory that the photosensitizer forms a complex with the reactant, the complex being the absorbing substance which decomposes under the action of light regenerating the sensitizer. Buchi²⁵ who has made a careful study of the sensitized decomposition of oxalic acid in the presence of uranyl sulphate considers that the absorbing constituent in the reaction is a complex of uranyl oxalate with oxalic acid. The reaction is not regarded as a

photosensitization in which uranyl sulphate absorbs light and transfers energy to oxalic acid on collision. In some cases this mechanism may be the one that is operative.

Mention should also be made of the work of Goodeve and Kitchener²⁶ who have utilized the hypothetical concept of 'exciton' of Frenkel²⁷ to explain the photosensitized oxidation of Sky Blue FF in the presence of solid titanium dioxide. The results of Goodeve and Kitchener can be explained on the hypothesis suggested by Gopalarao that the molecules of TiO_2 on the surface of the sensitizer oxidize the dye molecule under the action of light.

A review of the literature on photosensitization shows that the most common mechanism is the one which ascribes a chemical rôle to the activated photosensitizer molecule in an intermediate stage, though finally it is regenerated.

REFERENCES

- ¹ A. Eibner, *Chemiker. Zeitung* (1911), 35, 753, 774, 786.
- ² Kiedel, *Farben Zeitung* (1929), 34, 1242.
- ³ Wagner, *Farben Zeitung* (1929), 34, 1243, 35, 257.
- ⁴ Brocker, *Official Digest of Federation of Paint and Varnish Products Club* (1936), 153, 59.
- ⁵ Zellstoff. U. Papier (1935), 15, 496.
- ⁶ British Patents Nos. 430993, 448262, 449543.
- ⁷ *Official Digest of Fedn. of Paint and Varnish Products Club* (1936), 153, 59.
- ⁸ French Patent No. 793526, Jan. 27, 1936.
- ⁹ Brusilovski and Gorodetskaja, *Organ. Chem. Ind. U.S.S.R.* (1936), 2, 123.
- ¹⁰ Gopalarao and Dhar, *Soil Science* (1931), 31, 379.
- ¹¹ Gopalarao, *Soil Science* (1934), 38, 143.
- ¹² Gopalarao and Dhar, *J. Ind. Chem. Soc.* (1934), 11, 617.
- ¹³ Gopalarao and Pandalai, *J. Ind. Chem. Soc.* (1934), 11, 623.
- ¹⁴ Gopalarao and Varadanam, *Nature* (1938), 142, 618.
- ¹⁵ Dhar *et al.*, *Nature* (1936), 137, 629, 1000; 138, 648, 1060.
- ¹⁶ Gopalarao, *Zeit. fur. Physik. Chemie* (1939), 184, 377.
- ¹⁷ Franck and Haber, *Sintzungs berichte. Preuss Akad. d. Wiss.* (1931) 250.
- ¹⁸ Franck and Cario, *Z. Physik.*, 11, 161 (1922).
- ¹⁹ Compton and Turner, *Phil. Mag.*, 48, 360 (1924); *Phys. Review*, 25, 606 (1924).
- ²⁰ Dickinson, *Proc. Nat. Acad. Sci.* (1924), 10, 409.
- ²¹ Mitchell, *ibid.* (1925), 11, 458.
- ²² Rideal and Hirst, *Nature* (1925), 110, 899.
- ²³ Nordheim, *Z. Physik.* (1926), 36, 496.
- ²⁴ Winther, *Z. Wiss. Phot.*, 21, 175, (1922).
- ²⁵ Buchi, *Z. Physikal. Chem.* (1924), 111, 269.
- ²⁶ Goodeve and Kitchener, *Trans. Farad. Soc.* (1938), 34, 902.
- ²⁷ Frenkel, *Physik. Z. d. Sow.* (1936), 9, 158.

PHOTOSENSITIZATION BY STANNIC OXIDE SOL

By

CH. I. VARADANAM

Photosensitization by substances in the solid state is of great theoretical and practical interest. A. Eibner¹ studied the decolourization of various dyes in the presence of zinc oxide and light. C. Winther² observed the formation of hydrogen peroxide when water was exposed in a glass vessel to sunlight in the presence of zinc oxide. E. Baur³ and co-workers studied the decomposition of silver nitrate in aqueous solution in sunlight photosensitized by zinc oxide. Gopalarao and Dhar⁴ and Gopalarao⁵ observed that the oxidation of ammonia to nitrite in aqueous solution is markedly photosensitized by zinc oxide, titanium dioxide, uranic oxide, alumina, etc. Gopalarao and Pandalai⁶ have studied the photolysis of various amides and amines in sunlight in the presence of various photosensitizers. Gopalarao and Varadanam⁷ have found that ferric oxide is a good photocatalyst for the oxidative deamination of amino acids in sunlight.

In spite of the large amount of the work done on the phenomenon of photosensitization by solids, very little is known about the mechanism by which the photosensitizers act.

Recently Gopalarao⁸ carefully investigated the mechanism of photosensitized oxidation of ammonia with titania as photosensitizer. In this communication I am recording the results on the photosensitized oxidation of ammonia with colloidal stannic oxide.

Varadanam and Gopalarao⁹ found that stannic oxide acts as a good photosensitizer for the oxidation of ammonia in aqueous solutions. Stannic oxide was used in the colloidal condition in the experiments to be described in this paper.

Experimental.—The source of ultraviolet light is a Hereaus Quartz mercury vapour lamp worked on 220 volts D.C. mains at 3 amperes. The light is condensed and rendered parallel with the help of a quartz condenser on to the reaction cell, which is a quartz

cylindrical cell with two plane parallel sides of diameter 4 cm. The cell is fitted with a ground in stopper and has a capacity of 40 ml.

The hydrous stannic oxide colloid was prepared according to the method of Varadanam and Dhar¹⁰ which gives a highly concentrated sol. This was diluted and used in the experiments.

20 ml. of ammonia solution was put in the reaction cell, then the required quantity of the stannic oxide sol. was added and then water to make up the volume to 40 ml. After irradiation with ultra-violet light for the requisite time the colloid was coagulated by the addition of a small quantity of pure solid barium chloride and the nitrite content of the clear solution was estimated colorimetrically by the Griess-Ilosvay reaction.

TABLE I.

Influence of varying the amount of photosensitizer

Concentration of ammonia, N/2.

Time of exposure to total ultraviolet light, 6 hours.

Amount of SnO ₂ in grammes.	Milligrammes of nitrite nitrogen formed per litre.
Nil	..
0.00002	0.1210
0.00005	0.2524
0.00008	0.4923
0.00010	0.6691
0.00030	1.2170
0.00050	1.3250
0.00500	1.5530
0.01000	1.5530
0.02000	1.5550
0.05000	1.6420
0.20000	1.5220
0.30000	1.4710
0.60000	1.3010
0.72000	1.1580

It will be seen from the above table that at low concentrations there is observed an increase in the rate of ammonia oxidation proportionately to the increase in the amount of the photosensitizer; but as the concentration of the photosensitizer is increased further, the rate of oxidation of ammonia reaches a limiting value which, however, decreases slightly with a very large increase in the concentration of the photosensitizer.

TABLE II.

Influence of concentration of ammonia

Time of exposure to total ultraviolet light, 6 hours.

Amount of SnO_2 per 40 ml. of the solution, 0.02 grs.

Concentration of ammonia.	Milligrammes of nitrite nitrogen.
0.25 N	1.5550
0.125 N	1.3240
0.0625 N	1.0350
0.03125 N	0.8000
0.015625 N	0.6808
0.0078125 N	0.5793
0.00390625 N	0.4415
0.001953125 N	0.3112
0.0009765625 N	0.2333
0.00048828125 N	0.1296
0.000244140625 N	0.0649

The results show that for a very large change in the concentration of ammonia, the change in the rate of oxidation is only very slight. For instance, when the concentration is changed from 0.0625 N to 0.25 N (a change of 400%) the amount of nitrite nitrogen formed in six hours changes from 1.0350 to 1.5550 (a change of only 50%). If the reaction were a unimolecular one, there would have been observed a 400% change, instead of the 50% change actually obtained. The reaction thus appears to be zero molecular. It should be noted, however, that at very low concentrations of ammonia, a decrease in the rate of oxidation proportionately to the decrease in the concentration of ammonia is observed.

TABLE III

Progress of reaction with time

Concentration of ammonia, N/4.

Amount of SnO_2 per 40 ml., 0.02 grammes.

Time of exposure	Milligrammes of nitrite nitrogen formed
8 hours	2.214
16 "	4.375
24 "	6.628
32 "	8.871
40 "	10.630
48 "	13.340

The results indicate that the amount of nitrite nitrogen increases in proportion to the increase in the time of exposure.

Influence of Electrolytes.—The hydrous stannic oxide sol used in the experiment contains negatively charged miscelle and is coagulated by addition of suitable concentrations of positive ions like Na^+ , K^+ , NH_4^+ , Ba^{++} , Sr^{++} , etc., obtained from their salts. It has been suggested by Gopalarao¹ that the photosensitized oxidation of ammonia is a heterogeneous catalytic reaction occurring at the surface of the particles of the photosensitizer. Any factor tending to reduce the effective surface should bring about a decrease in the rate of the reaction. It is well known that in the coagulation of a sol by a neutral salt there is agglomeration of the smaller colloidal particles into bigger particles which ultimately settle down under the action of gravity. During such agglomeration and coagulation the effective surface is very much reduced. As this is a photochemical reaction we should select such salts which do not otherwise interfere with the absorption of light. In the following tables are reported the results on the influence of different ions.

TABLE IV

Influence of Monovalent Cations

Grammes of SnO_2 per 40 ml., 0.01. Concentration of ammonia, N/8.
Time of Exposure, 8 hrs.

Na^+ from NaCl		Na^+ from Na_2SO_4		K^+ from KCl		NH_4^+ from NH_4Cl	
Concentration	Milli-grams of nitrite nitrogen	Concentration	Milli-grams of nitrite nitrogen	Concentration	Milli-grams of nitrite nitrogen	Concentration	Milli-grams of nitrite nitrogen per litre
Nil	1.75	Nil	1.75	Nil	1.75	Nil	1.75
$2.5 \times 10^{-2}\text{N}$	1.652	$2.5 \times 10^{-2}\text{N}$	$5.0 \times 10^{-2}\text{N}$	1.626
$7.5 \times 10^{-2}\text{N}$	1.546	$7.5 \times 10^{-2}\text{N}$	1.672
$12.5 \times 10^{-2}\text{N}$	1.442	$12.5 \times 10^{-2}\text{N}$	1.562	$10 \times 10^{-2}\text{N}$	1.652	$12.5 \times 10^{-2}\text{N}$	1.482
$17.5 \times 10^{-2}\text{N}$	1.381	$17.5 \times 10^{-2}\text{N}$	1.462	$17.5 \times 10^{-2}\text{N}$	1.584	$17.5 \times 10^{-2}\text{N}$	1.389
$25.0 \times 10^{-2}\text{N}$	1.287	$25.0 \times 10^{-2}\text{N}$	1.346	$25.0 \times 10^{-2}\text{N}$	1.492	$25.0 \times 10^{-2}\text{N}$	1.265
$37.5 \times 10^{-2}\text{N}$	1.275	$37.5 \times 10^{-2}\text{N}$	1.292	$37.5 \times 10^{-2}\text{N}$	1.395	$37.5 \times 10^{-2}\text{N}$	1.254
$50.0 \times 10^{-2}\text{N}$	1.272	$50.0 \times 10^{-2}\text{N}$	1.272	$50.0 \times 10^{-2}\text{N}$	1.321	$50.0 \times 10^{-2}\text{N}$	1.245
$100.0 \times 10^{-2}\text{N}$	1.278	$100.0 \times 10^{-2}\text{N}$	1.267	$100.0 \times 10^{-2}\text{N}$	1.330

TABLE V

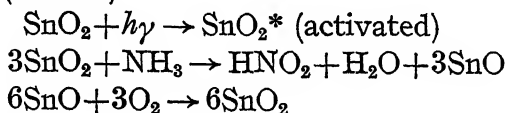
Influence of Polyvalent Cations

Concentration of ammonia, N/8. Time of Exposure, 8 hrs.

Grammes of SnO_2 per 40 ml., 0.01.

Ba^{++} from BaCl_2		Sr^{++} from SrCl_2		Al^{+++} from AlCl_3	
Concentration	Milli-grammes of nitrite nitrogen	Concentration	Milli-grammes of nitrite nitrogen	Concentration	Milli-grammes of nitrite nitrogen
Nil	1.750	Nil	1.750	Nil	1.750
25×10^{-6} Molar	1.556	25×10^{-6} Molar	1.523	5.0×10^{-4} Molar	1.163
75×10^{-6} "	1.462	75×10^{-6} "	1.441	15.0×10^{-4} "	1.025
125×10^{-6} "	1.286	125×10^{-6} "	1.238	25.0×10^{-4} "	0.912
175×10^{-6} "	1.103	175×10^{-6} "	1.065	35.0×10^{-4} "	0.720
250×10^{-6} "	0.843	250×10^{-6} "	0.812	35.0×10^{-4} "	0.720
375×10^{-6} "	0.824	375×10^{-6} "	0.785	50.0×10^{-4} "	0.399
500×10^{-6} "	0.814	500×10^{-6} "	0.764	75.0×10^{-4} "	0.219
2500×10^{-6} "	0.819	2500×10^{-6} "	0.756	100.0×10^{-4} "	0.162
5000×10^{-6} "	0.812	5000×10^{-6} "	0.759

Discussion of Results.—It appears that in the presence of air and light the photosensitized oxidation of ammonia in the presence of stannic oxide occurs according to the mechanism suggested by Gopalarao (*loc. cit.*).



A molecule of stannic oxide gets activated by the absorption of a quantum of light. The activated stannic oxide then oxidizes ammonia to nitrous acid getting itself reduced to lower oxide. The latter then undergoes oxidation by the dissolved oxygen. The lower oxide may be Sn_2O_3 instead of SnO .

In the presence of a constant amount of photosensitizer, stannic oxide and a constant intensity of light, we can presume that the number of activated stannic oxide molecules will be fairly constant. Therefore, the rate of reaction and its order depends only on the active mass or concentration of the ammonia molecules at the surface of stannic oxide. The active mass is not the simple concentration of the ammonia in the homogeneous solution phase. The

amount of substance adsorbed and therefore in a position to react is the real active mass.

Let us assume with Langmuir, that the molecules of ammonia adsorbed on the surface of stannic oxide form a unimolecular layer. The adsorbent is represented by a crystal lattice in the interior of which all valencies are saturated while at the surface this is not the case. Langmuir assumes that the unsaturated valencies are responsible for the adsorption. These projected valencies are, however, distributed regularly over the surface and form adsorbing spaces in that surface. Molecules coming within the sphere of attraction of these spaces are adsorbed, but owing to their kinetic energy which acts in the opposite sense, they tend to escape; hence we have simultaneously 'condensation' and 'evaporation' on the surface. A state of equilibrium is established as soon as the rate of condensation per unit surface is balanced by the rate of evaporation. Let θ represent the fraction of the total number of available spaces occupied per unit area of surface; then $1 - \theta$ is the part unoccupied. The rate of condensation will be proportional to the fraction of surface unoccupied and to the number of molecules (m) colliding per second per unit area, which number is proportional to the concentration (C) in the solution phase.

$$\begin{aligned}\text{Rate of condensation} &\propto m(1 - \theta) \\ &\propto C(1 - \theta) \\ &= K_1 C(1 - \theta)\end{aligned}$$

$$\text{Rate of evaporation} = K_2 \theta$$

where K_2 is the rate at which the substance would evaporate if all available spaces were completely covered up. When the substance in solution is in equilibrium with the surface, the rate of evaporation must be equal to the rate of condensation.

$$\begin{aligned}K_1 C(1 - \theta) &= K_2 \theta \\ \frac{K_1}{K_2} C(1 - \theta) &= \theta\end{aligned}$$

$$\text{Expanding and rearranging, } \frac{K_1}{K_2} C = \theta + \frac{K_1}{K_2} C \theta$$

$$\frac{K_1}{K_2} C = \left(1 + \frac{K_1}{K_2} C\right) \theta$$

from which we get,

$$\theta = \frac{K_1}{K_2} C / 1 + \frac{K_1}{K_2} C.$$

If we make $\frac{K_1}{K_2} = K_3$ (constant), then we have,

$$\theta = \frac{K_3 C}{1 + K_3 C}.$$

The number of molecules adsorbed and hence the amount of substance adsorbed (X) is proportional to θ ; we can substitute (X) for θ and combine the new proportionality factor with K_3 and obtain another constant K_4 , whence

$$X = \frac{K_4 C}{1 + K_3 C}.$$

This equation gives us a relation between the amount (X) of ammonia adsorbed and the equilibrium concentration C. For very low concentrations, $K_3 C$ in the denominator becomes negligible compared to unity so that

$$X = K_4 C \dots \dots \dots (\text{Case I})$$

$$X = \frac{K_4 C}{K_3 C} = \frac{K_4}{K_3} = \text{Constant} \dots \dots (\text{Case II}).$$

Thus we have that,

when adsorption is small the amount adsorbed is directly proportional to the concentration (case I). When adsorption is strong (case II), the amount adsorbed is practically constant and independent of concentration.

Hence in the photosensitized oxidation of ammonia in the presence of stannic oxide, we have to note that it is the active mass of the substance in the adsorbed layer that determines the rate and order of reaction.

From the above equation (case II) we find that when adsorption is strong the amount of substance adsorbed is practically independent

of the concentration in the bulk of the solution. Hence the rate of reaction will be independent of concentration and time; the reaction thus becomes one of zero order. This result has been obtained in the present case. The results in table II show that when the concentration is changed from 0.0625 N to 0.25 N (a change of 400%) the reaction rate changes by only 50%. If the reaction were a unimolecular one, there would have been observed a 400 % change.

However, when the concentration is sufficiently reduced (below 0.0009765625 N) the reaction rate will be no longer independent of concentration and the zero order reaction passes into one of the unimolecular type. It can be seen from table II that the reaction rate with 0.0009765625 N is double the reaction rate obtained with 0.00048828125 N and this again is double the rate obtained with a solution of ammonia of concentration 0.000244140625 N. The reaction is thus of zero order at high concentrations of ammonia and unimolecular at low concentrations. This behaviour is satisfactorily explained by the mechanism suggested above.

That the reaction is a heterogeneous one occurring at the surface of stannic oxide is shown by the fact, that agglomeration of the colloidal particles, with consequent reduction of the total surface brought about by the addition of electrolytes results in a decrease in the reaction rate (vide tables IV and V). With any one electrolyte, increasing concentration causes a progressively diminishing rate until a steady limiting rate is reached. This is obtained when the sol is coagulated. After the coagulation point, a further increase in the concentration of the electrolyte does not produce a further diminution in the reaction rate. The concentration that produces the limiting reaction rate is approximately the same with Na^+ (from NaCl and Na_2SO_4), K^+ (from KCl), and NH_4^+ (from NH_4Cl). It should be noted that the concentration of divalent ions Ba^{++} and Sr^{++} required to lower the reaction rate to the limiting value is much lower than with univalent Na^+ , K^+ , or NH_4^+ ions. Further, it is significant that the limiting rate with divalent ions is lower than that with univalent ions.

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REFERENCES

- ¹ A. Eibner, *Chemiker Zeitung* (1911).
- ² C. Winther, *Z. Wiss. Phot.* (1921), 21, 141, 168, 175.
- ³ E. Baur, *Helv. Chim. Acta.* (1918), 1, 186; (1927), 10, 901.
- ⁴ G. Gopalarao and N. R. Dhar, *Soil Science* (1931), 31, 379.
- ⁵ G. Gopalarao, *Soil Science* (1934), 38, 143.
- ⁶ G. Gopalarao and K. M. Pandalai, *J. Ind. Chem. Soc.* (1934), 11, 623.
- ⁷ G. Gopalarao and Ch. I. Varadanam, *Nature* (1938), 142, 618.
- ⁸ G. Gopalarao, *Zeit. Fur. Physik. Chem.* (1939), 184A, 377.
- ⁹ Varadanam and Gopalarao, *Current Science* (1938), 7, 231.
- ¹⁰ Varadanam and Dhar, *J. Ind. Chem. Soc.* (1936), 13, 602.

SOME NEW ANALYTICAL METHODS

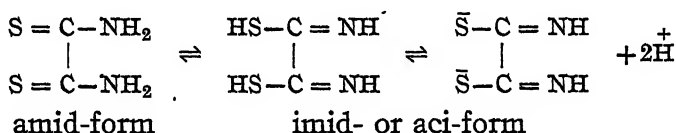
By

PRIYADARANJAN RAY

In this article it is intended by the writer to review some analytical methods which were developed from time to time in his laboratory at the College of Science and Technology, University of Calcutta.

I. *Rubeanic Acid*

Rubeanic acid, as its formula indicates, can exist in solution in two tautomeric forms in equilibrium, which may be regarded as symmetrical dithio-oxamide and symmetrical di-imido-dithio-oxalic acid. Only the latter can behave as an acid.

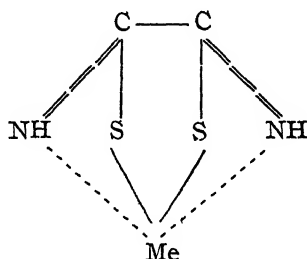


Evidently, the equilibrium will be greatly influenced by hydrogen ion concentration in favour of the normal or amid-form. With hydroxyl ion, therefore, the opposite will hold good, i.e., the aci-form will preponderate. This is fully borne out by its behaviour towards copper, nickel and cobalt ions.

Copper rubeanate, being highly insoluble, is precipitated even in acid solutions, whereas cobalt and nickel compounds do not separate unless the solution is rendered alkaline with ammonia or alkali; once precipitated, however, they are almost as insoluble as the copper compound.

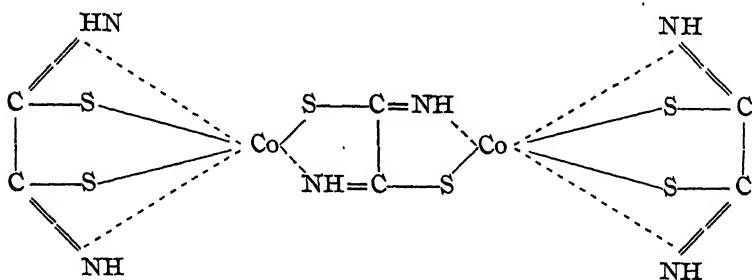
The aci-form of rubeanic acid may be regarded as a tetradentate group, giving rise with copper, nickel and cobalt ions to inner-metallic complexes of the following type: the sulphur atoms of the two HS-groups furnish the primary valencies and the nitrogen atoms

of the two NH-groups supplying the auxiliary valencies for the central metallic atom. This gives rise to the formation of two interpenetrating five-membered rings with the four covalent metal atom as the common link. The aci-form of rubeanic acid reacts here in its cis-structure.



where Me = Cu, Co or Ni.

Dübsky and Trtilek have recently shown that in the cobalt compound the cobalt atom usually functions as a tervalent element; hence the metal atom should behave as one of a six-covalent type, hexa-co-ordination being a characteristic of all complexes with tervalent central atom. In this latter case, the formula for the cobalt rubeanate may be represented as a binuclear inner-metallic complex depicted below.



An aci-form of rubeanic acid in its trans-structure probably furnishes the bridge linkages between the two cobalt atoms.

It might, however, be suggested that the metal rubeanates are merely simple salts, the rubeanic acid serving only as a dibasic acid in its aci-form like oxalic acid. But intense characteristic colour, extreme insolubility in water, aqueous ammonia and acids, as well

as the other properties of these substances are strongly suggestive of their complex character.

Copper rubeanate forms dark, greenish black, insoluble precipitate unaffected by dilute acids, alkalies or ammonia. In extremely dilute solutions a dark green colour is produced. One part of copper in one million parts of water is immediately precipitated by the reagent, while by means of the colour-effect copper can be detected in a dilution of even one in 30 million parts of water. In fact, the reagent is so sensitive that the solubility of metallic copper in boiling distilled water can be demonstrated by its use.

Nickel rubeanate forms violet-blue precipitate insoluble in water, dilute acids, alkalies or ammonia. It dissolves, however, in pyridine to a pink-coloured solution. With strong ammonia it forms a deep orange-red solution, from which the violet-blue rubeanate is reprecipitated by dilution with water. Unstable hexa-co-ordinated nickel complexes are probably formed in these cases. One part of nickel in 500,000 parts of water (alkaline) is immediately precipitated by the reagent, and the blue-violet colour-effect enables the detection of one part of the metal in seven million parts of water.

Cobalt rubeanate gives rise to a reddish brown precipitate, insoluble like the corresponding nickel compound in water, dilute acids, alkalies or ammonia. It is, however, unaffected by strong ammonia. One part of cobalt in 150,000 parts of water (alkaline) is immediately precipitated by the reagent, while cobalt in a dilution of one in 30 million can be detected by the yellow colouration developed.

Both nickel and cobalt can be estimated quantitatively by precipitation as rubeanate, the former being converted to nickel oxide by ignition and the latter to cobalt sulphate by heating with conc. sulphuric acid.

Processes for the colorimetric estimation of nickel, cobalt and copper have been developed by the use of suitable colloids as peptizing agents for the metal rubeanates.

Sensitivity of the reactions with rubeanic acid can be considerably heightened by working with silk threads, capillaries, or,

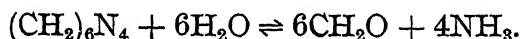
on impregnated spot papers according to Feigl and on impregnated gelatine according to Winckelmann.

Feigl has also shown that with the help of spot reaction copper can be detected by means of rubeanic acid in presence of cobalt or nickel in one and the same solution. When the reaction is carried out on a spot paper, greenish black ring of copper is developed surrounded by blue or yellow rings of nickel or cobalt due to capillary separation.

Rubeanic acid has been used by Wölbling and Steiger as a reagent for the detection of ruthenium which gives a blue colouration in hydrochloric acid solution, and also for the quantitative determination of palladium which forms a red precipitate in acid solution.

II. *Hexamethylene tetramine—Hexamine*

Hexamethylene tetramine $(\text{CH}_2)_6\text{N}_4$, whose aqueous solution reacts almost neutral to litmus, is, however, hydrolyzed in acid solutions into formaldehyde and ammonia, according to the following scheme :



Presence of H^+ -ion as a catalyst is necessary for inducing this reaction. The liberated ammonia combines with the H^+ -ion of the acid or water to form NH_4^+ , which leads to a rise in the hydroxyl ion concentration of the solution. This can, however, to a certain extent be modified or controlled by the addition of ammonium ions in the form of ammonium salts. Since NH_4^+ -ions, by combining with OH^- -ions to form undissociated ammonium hydroxide, NH_4OH , will tend to oppose this rise.

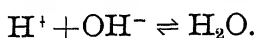
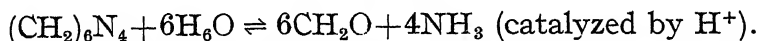
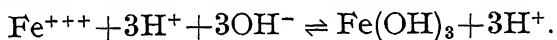
This behaviour of hexamine has been utilized for the quantitative separation of iron, aluminium, titanium, uranium, zirconium and thorium from metals of group IIIB (analytical) and magnesium, based on the increased hydrolysis of the salts of tervalent metals in aqueous solution.

The quantity of ammonia liberated by hexamine is dependent upon the amount of acids, or H^+ -ion concentration, in a solution. Salts of tervalent metals like iron, aluminium, chromium and of

quadrivalent metals like titanium, zirconium and thorium are hydrolyzed more or less in aqueous solution with liberation of free acids. In an aqueous solution of these salts, therefore, hexamine behaves to a certain extent as ammonium hydroxide, though the quantity of the latter formed is determined by the extent of hydrolysis of the metal salt in any particular case. As a matter of fact, the effective concentration of ammonium hydroxide, or of free OH^- -ion, that can be formed in the solution at any moment, is hereby restricted. Addition of a sufficient quantity of an ammonium salt to the solution further accentuates this restriction. It has been observed that iron, aluminium, chromium, titanium, uranium, zirconium and thorium can be completely precipitated from solutions of their salts by boiling with a solution of hexamine. Under the same conditions manganese, zinc, nickel, cobalt and magnesium are only partially precipitated, since, in their case, the ammonium salts, gradually formed in the solution during the reaction, prevents unrestricted lowering of H^+ -ion concentration. It was also found that by the previous addition of a sufficient amount of ammonium salts the precipitation of the hydroxides of these latter metals could be completely avoided even from the boiling solutions; on the other hand, the hydroxides of iron, aluminium, chromium, titanium, uranium, zirconium and thorium were quantitatively precipitated. This led to the development of a method for a satisfactory quantitative separation of these metals from the above-mentioned bivalent ones.

The behaviour of the solution of salts of various metals towards hexamine is in perfect accord with the conclusions that might be deduced from the respective solubility product of their hydroxides and pH-values at which these commence to separate. In addition to its effect upon H^+ - and OH^- -ion concentration of the solution, ammonium chloride also aids in the separation to a certain extent by favouring the formation of complex metal-ammonium ions from the bivalent metal ions and the free ammonia resulting from the hydrolysis of hexamine. A large excess of ammonium ions due to ammonium chloride retards the dissociation of ammonium hydroxide and favours the retention of free ammonia in the solution.

The removal of hydrogen ions leading to the precipitation of tervalent metal hydroxides can be represented by the following equations for ferric ion, for instance :



Iron can be satisfactorily separated from zinc, manganese, nickel, cobalt and magnesium by a single precipitation with hexamine in presence of ammonium salts. The method, however, fails in the case of chromium, as the precipitate of chromium hydroxide is always contaminated with some hydroxides of the bivalent metals. This is possibly due to the marked tendency of chromium hydroxide to form chromites or compounds of the spinel type, such as $\text{XO} \cdot \text{Cr}_2\text{O}_3$ (X = an atom of a bivalent metal).

Aluminium, when present as chloride or nitrate, cannot be completely precipitated from solution by hexamine even at the boiling temperature. Addition of sulphate ions, however, leads to a complete precipitation. This might be attributed to the increased hydrolysis of the sulphate and the formation of insoluble basic sulphate. Under these conditions aluminium can be separated quantitatively from magnesium, manganese, cobalt and small quantities of zinc. Separation from nickel, however, does not succeed even by double precipitation. Possibly the formation of an adsorption compound or a compound of the spinel type constitutes the disturbing factor.

Uranium and zirconium present no difficulties in their separation from the bivalent metals by hexamine. The same holds good also for thorium, provided the solution does not contain any sulphate ion, as the latter has been found to retard in a great measure the precipitation of thorium hydroxide by hexamine, apparently through the formation of complex sulphate.

Titanium, whose salts are extensively hydrolyzed in aqueous solution, can be separated easily from magnesium, manganese, nickel, cobalt and small quantities of zinc.

Solutions of lanthanum salts give no precipitate with hexamine in the cold and only a slight turbidity even at the boiling temperature. In presence of sulphate ions, however, a partial precipitation of lanthanum hydroxide occurs from the boiling solution. A large excess of ammonium chloride, on the other hand, hindered the precipitation.

Solutions of cerium, praseodymium and neodymium salts give no precipitate with hexamine in the cold, but a partial precipitation occurs at the boiling temperature. Addition of an excess of ammonium salts retard this precipitation to a great extent.

Solutions of yttrium salts, when treated with hexamine, give no precipitate in the cold, but complete precipitation occurs from the boiling solution even in the presence of much ammonium chloride.

Separation of thorium from cerium, lanthanum, praseodymium, neodymium and yttrium by double precipitation with hexamine in the cold (30°C.) has been described by Ismail and Harwood.

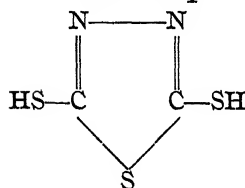
Hexamine has been recommended for the separation of iron from barium, strontium and calcium in preference to ammonia, as the latter is often contaminated with ammonium carbonate formed by the absorption of atmospheric carbon dioxide.

The hexamine method of separation in certain cases offers decided advantages over the earlier barium carbonate and the basic acetate methods, as well as over many others recently introduced.

III. *Dimercaptothiobiazole*

Dimercaptothiobiazole, or thiobiazole—1:4 dithiol, has been found to be a very convenient reagent for the estimation of copper, lead and bismuth, and for their separation from the metals of the group IIB and the remaining analytical groups (e.g., As, Sb, Sn, Mo, Fe, Zn, etc.). The substance also serves as a very sensitive micro-reagent for the detection of bismuth and copper.

Dimercaptothiobiazole behaves as a very weak acid like H_2S , the hydrogen atoms of the sulphydryl groups being replaced by



metals under suitable conditions. It gives characteristic coloured precipitates with solutions of the salts of most of the elements of the hydrogen sulphide group of the analytical table. As the precipitates obtained are mostly of variable composition, they could not be directly weighed.

The reagent can be easily prepared from carbon disulphide and hydrazine hydrate in alcoholic ammonia according to the method described by Losanitsch. A solution of the ammonium salt of the reagent is used for analytical purposes.

An aqueous solution of the reagent gives with the hydrochloric acid solution of copper salts an insoluble brown precipitate. Precipitation limit = 1 in 1,600,000; colouration limit = 1 in 1,650,000.

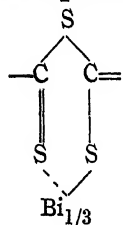
For the purpose of quantitative estimation, the copper precipitate was decomposed with nitric acid and the copper was estimated iodometrically in the solution. The method permits the separation of copper from iron, zinc, arsenic, antimony, tin, molybdenum and tungsten under suitable conditions with ammonium fluoride as a masking agent for arsenic and antimony, and tartaric acid for tin. The other metals of group III (analytical) and the metals of the succeeding groups do not interfere with the precipitation of copper.

Lead is precipitated from a solution containing tartaric acid or acetic acid in the form of a dense, bright yellow powder. The precipitate is converted into lead sulphate by heating with nitric acid and sulphuric acid in a crucible and then weighed as such. Lead can be separated in this way from tin and molybdenum in slightly acid solution in presence of ammonium tartrate. Separation from antimony can be effected in slightly ammoniacal solution by the addition of ammonium fluoride and tartrate. Separation of lead from alkaline earth metals by this reagent present no difficulties at all.

Bismuth in nitric acid solution gives a bright scarlet precipitate with dimercaptothiobiazole. This is a very sensitive and specific reaction which enables the detection of bismuth in presence of all other elements excepting copper. The effect of other possible interfering elements, such as lead, arsenic, tin, antimony and mercury, which also give coloured precipitates with the reagent, can be

neutralized by suitable adjustment of the conditions of precipitation. Alkali fluoride can be used as a masking agent for arsenic, antimony and tin. The precipitation limit for bismuth = 1 part in 200,000 parts, colouration limit = 1 part in 1,000,000 parts.

Dübsky and co-workers, who have carried out an extensive investigation on the use of cyclic compounds containing mercapto-groups for analytical purposes, specially for the identification of bismuth, have named the reagent as Bismuthiol I. They regard the scarlet bismuth precipitate as a non-electrolyte inner-metallic complex as shown below.



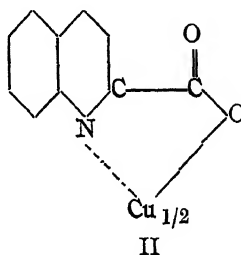
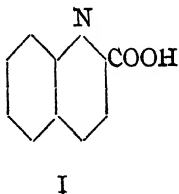
Dübsky and Okâc obtained a much lower value for sensitivity of the bismuth reaction as they employed hydrochloric acid solution, in which the bismuth precipitate is slightly soluble. The value for sensitivity, as given by them, is 1 in 28,000 only.

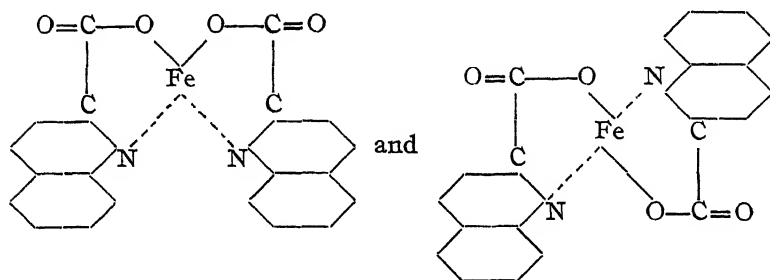
From solutions rendered faintly acid with acetic or tartaric acid bismuth can be separated by this reagent from arsenic, antimony, tin and molybdenum with the use of tartaric acid or ammonium fluoride as masking agents.

IV. Quinaldinic Acid

Quinaldinic acid (I) has been introduced with great success for the estimation of copper, cadmium and zinc and for their separation from many metals. It has been employed for the colorimetric estimation of iron and for the gravimetric determination of uranium.

In the case of copper and ferrous iron it is believed that insoluble, characteristic, inner-metallic complexes with formation of





III

(a) Cis-(red).

(b) Trans-(blue-violet).

five-membered rings (II and III) are produced, in which the metal atom co-ordinates with the nitrogen atom, replacing at the same time the hydrogen atom in the carboxyl group of quinaldine acid.

Interesting observations have, however, been made in the case of ferrous compound. When precipitated in the cold, it first forms a dark red, comparatively more soluble precipitate which soon, specially by rise of temperature, changes into a difficultly soluble, blue-violet modification. It is apparent that the two forms are related to each other as cis-trans isomers, due to the planar configuration of the tetra-co-ordinated ferrous complex [III (a) and (b)]. In (a) the two N-atoms occupy adjacent positions, in (b) they are diagonally situated. The unstable red modification corresponds to the cis-form and the stable blue-violet variety represents the trans-form.

Quinaldine acid serves as an excellent reagent for the estimation of copper. The sensitivity of the reaction is very great and far exceeds that of other reagents.

Turbidity limit:—1 part in 20 million parts.

Precipitation limit:—1 part in 2.5 million parts.

Copper is completely precipitated in dilute mineral acid solutions. The bluish green precipitate, dried at 125°C., has the composition, $\text{Cu}(\text{C}_{10}\text{H}_6\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, in which form it is weighed. In mineral acid solutions copper can be separated from Cd, Pb, As, P, Ni, Co, Mn, Mg and alkaline earths. For separation from lead, the solution should, however, be acidified with acetic acid and must not contain

any chlorine or sulphate ions. The method has also been adapted for the micro-estimation of copper.

Zinc is quantitatively precipitated from dilute acetic acid solution by sodium quinaldinate. The white zinc precipitate, dried at 125°C ., has the composition, $\text{Zn}(\text{C}_{10}\text{H}_6\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, and is directly weighed in this form. Manganese, magnesium, phosphoric acid, arsenic or arsenious acid and the alkaline earths do not interfere with the estimation. From a faintly alkaline solution containing a sufficient quantity of tartrate zinc can be estimated quantitatively as quinaldinate in the presence of Fe, Al, Be, U and Ti. This procedure, however, fails in the presence of chromium, which has a tendency to hold back some zinc in solution, and the results obtained are always 2-3% too low. Zinc has also been estimated in acetic acid solution in the presence of copper, mercury and silver by the previous addition of thiourea as a masking agent. Thiourea is known to form quite stable complexes with Cu^+ , Hg^{++} and Ag^+ ions. Copper is first reduced to cuprous state by means of sodium bisulphite in dilute acetic acid solution. In the presence of silver or mercury, or both, besides copper, the solution should be first treated with an excess of potassium iodide before the addition of bisulphite, in order to prevent the reduction of mercury and silver salts to the metallic state. Potassium iodide converts the mercury into complex mercuri-iodide and precipitates the silver as silver iodide, which are not affected by sulphur dioxide. Silver iodide is, however, easily soluble in thiourea. These methods have also been adapted for the micro-estimation of zinc.

Quinaldinic acid has also been utilized for the colorimetric estimation of zinc by Lott who used nitro-quinaldinic acid for the precipitation of zinc. The solution of zinc precipitate in dilute acids on treatment with stannous chloride gives an intense yellow colouration.

Ferrous ion in very dilute neutral solution gives a pale red and in comparatively stronger solution a dark-red colouration with sodium quinaldinate. The colour is intensified by the addition of a dilute potassium cyanide solution. For the reduction of any ferric iron, the solution is first treated with a little hydroxylamine hydro-

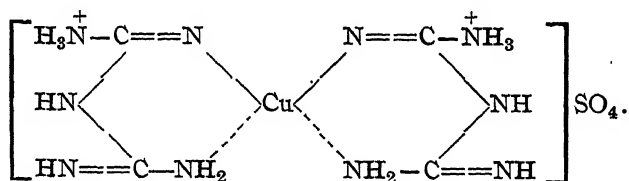
chloride. Iron can thus be estimated colorimetrically in the presence of a fairly large quantity of copper, nickel, cobalt, zinc, etc. The sensitivity of the reaction = 1 part in 14.5 million parts.

Cadmium is precipitated quantitatively as a white powder from almost neutral solutions ($\text{pH} = 5$) by sodium quinaldinate in the cold. The precipitate is dried at 150°C . The weight of cadmium is calculated from the formula, $\text{Cd}(\text{C}_{10}\text{H}_6\text{NO}_2)_2$.

The reagent is prepared from quinaldine according to the method described by Hammick. It can be recovered without difficulty from its cadmium, zinc and copper salts.

V. Biguanide Sulphate

Biguanide sulphate is long known to form a sparingly soluble copper biguanide sulphate in ammoniacal copper salt solution. The constitution of metal-biguanide complexes has been thoroughly discussed in a number of papers published from this laboratory. Copper biguanide sulphate can be represented as an inner-metallic complex salt of the second order as shown below.



It forms a pink-coloured precipitate, whose solubility in water at or below 10°C . is almost negligible. The precipitate, when washed with alcohol and ether, and then dried at 50° – 60°C ., has the composition, $[\text{Cu}(\text{BigH})_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, where BigH = a molecule of biguanide. In this form it can be directly weighed.

An elegant method for the estimation of copper and for its separation from zinc, cadmium, molybdenum and tungsten has thus been developed. The estimations have been carried out both on the macro- and semi-micro scale with excellent results.

The reagent has also been utilized for the volumetric estimation of copper, using rubeanic acid as an external indicator. Zinc and tungsten do not interfere.

Most of the above-described reagents are now placed on the market by several German, American and British firms.

REFERENCES

- I. Rubeanic Acid.
Rây and Ray, J. Indian Chem. Soc., 1926, 118.
Rây, Zeit. anal. Chem., 79, 1929, 94.
Dübsky and Trtilek, Mikrochemie, 23, 1937, 38.
Feigl and Kapulitzas, Mikrochemie, 8, 1930, 239.
Wölbling and Steiger, Mikrochemie, 15, 1934, 295.
For the preparation of Rubeanic Acid, see Wollner, J. Pr. Chem., 29, 1884, 129.
- II. Hexamine.
Rây and Chattopadhyaya, Z. anorg. u. allg. Chem., 169, 1928, 99.
Rây, Zeit. anal. Chem., 86, 1931, 13.
Ismail and Harwood, Analyst, 62, 1937, 185.
- III. Dimercaptothiobiazole.
Rây and Gupta, J. Indian Chem. Soc., 1935, 308.
Dübsky and Okác, Z. anal. Chem., 96, 1934, 267.
Losanitsch, J. Chem. Soc., 121, 1922, 2544.
- IV. Quinaldinic Acid.
Rây and Bose, Z. anal. Chem., 95, 1933, 400.
Rây and Majumdar, *ibid.*, 100, 1935, 324.
Rây and Dutt, *ibid.*, 115, 1938, 265.
Rây and Bose, Mikrochemie, 17, 1935, 11; 18, 1935, 89.
Rây and Gupta, *ibid.*, 17, 1935, 14.
Rây and Sarkar, *ibid.*, 27, 1939, 64.
Lott, Industrial and Engineering Chem. (analyt. ed.), 10, 1938, 335.
Majumdar, Analyst, 64, 1939, 874.
Hammick, J. Chem. Soc., 123, 1923, 2882.
- V. Biguanide Sulphate.
Rây and Ray Chaudhury, J. Indian Chem. Soc., 1941, 149
See also Rây and Co-workers, J. Indian Chem. Soc., 1937, 670; 1938, 350, 353; 1939, 621, 629, 617.

OXIDATION-REDUCTION INDICATORS IN VOLUMETRIC ANALYSIS

By

K. NEELAKANTAM

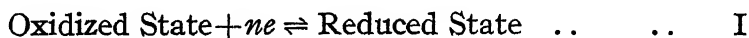
Oxidizing agents available in volumetric analysis are three in number, namely, permanganate, dichromate and ceric sulphate. Potassium permanganate by virtue of its high standard oxidation potential (hereafter denoted by S.O.P.) in sulphuric acid solution (1.45 volts)* and its readily visible purple colour is a very delicate oxidizing agent. Although most widely used, in actual practice it suffers from several disadvantages, one of which is that it could not be used in iron titrations in presence of hydrochloric acid without adopting special procedures. Potassium dichromate (S.O.P. 1.12 volts in acid solution), though a less powerful oxidant than permanganate, possesses certain advantages over the latter. It can be used for titrating ferrous ions in presence of hydrochloric acid, but it suffers from the defect that it must always be used with an indicator, external or internal. Ceric sulphate (S.O.P. 1.60 volts) is in general comparable with permanganate and in fact possesses certain advantages over it. Its chief drawback, however, is that it cannot serve as its own indicator except in a few titrations and must, therefore, be used with an indicator.

It was early recognized that if suitable indicators could be found for the less frequently used but much more advantageous oxidants, dichromate and ceric sulphate, they would become very valuable in oxidation-reduction titrations. Investigations carried out had, therefore, primarily the object of finding suitable indicators for use with these two oxidants and secondarily for use with permanganate, especially in ferrous titrations in presence of hydrochloric acid, and in titrations with very dilute oxidant. The introduction

* All potentials are given on the basis of the normal hydrogen electrode throughout this article.

of diphenylamine by Knop in 1924 stimulated interest in these indicators and to-day we have, as a result, a large number of them.

An oxidation-reduction indicator is a substance which has different colours in the oxidized and reduced (normal) states, generally coloured and colourless respectively with a few exceptions. Such indicators may be reversible or irreversible. Though some indicators which are not strictly reversible have been used, the former type are the most important. With a reversible indicator, the oxidized and reduced forms together constitute a reversible oxidation-reduction system. The relationship between the oxidized and reduced states of such a system is represented by the following equation:—



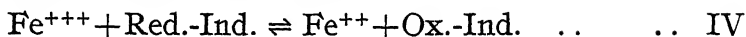
wherein n represents the difference in the number of electrons and e stands for the electron. If the system is thermodynamically reversible, then the potential (E) acquired by an unattackable electrode (e.g., platinum) placed in the solution will be given by

$$E = E_0 + \frac{RT}{nF} \log e \frac{[\text{Ox.-Ind.}]}{[\text{Red.-Ind.}]} \quad \dots \quad \text{II}$$

where E_0 is a constant, called the standard oxidation potential (S.O.P.) of the system, R , T , F and n have the usual significance, the square brackets indicate the concentrations, and Ox.-Ind. and Red.-Ind. stand for the oxidized and reduced forms of the indicator respectively. A small change in the value of E will bring about a corresponding change in the value of $\log e \frac{[\text{Ox.-Ind.}]}{[\text{Red.-Ind.}]}$ which in its turn will be indicated by a change in the depth of colour. Every depth of colour of the indicator, therefore, corresponds to a definite potential. When such an indicator is added to any oxidation-reduction system such as, for example, a mixture of ferric and ferrous ions which constitutes a reversible system for which a similar equation

$$E = \frac{E_0}{\text{Fe}^{+++}, \text{Fe}^{++}} + \frac{RT}{nF} \log e \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} \quad \dots \quad \text{III}$$

holds, the following reaction takes place—



no account being taken of the influence of $[\text{H}^+]$. Thermodynamically this reaction should take place until the respective potentials of the two systems, $\text{Ox.-Ind.} \rightleftharpoons \text{Red.-Ind.}$, and $\text{Fe}^{+++} \rightleftharpoons \text{Fe}^{++}$ ions are equal. The indicator, therefore, adjusts itself so that its potential is the same as that of the solution in which it is placed. In the course of a titration of a solution consisting almost exclusively of the reduced form of a given system, for example, ferrous ions with an oxidant, the ratio of the concentrations of the oxidized and reduced states increases and the potential of the unattackable electrode increases rapidly at first, then slowly, and finally rapidly again when the oxidation is almost complete. Since the potential of the indicator system itself varies in an identical manner simultaneously, to obtain an end-point the potential at which the colour change takes place should lie between the oxidation potentials of the two reacting systems, oxidant and reductant. The potential at which the colour change takes place may be deduced thus: From the equation II it is evident that if the indicator is 50% oxidized, E_0 (S.O.P.) becomes equal to E . Similarly, it can be shown that when $E = E_0 + 0.05$ volt, the indicator shows practically its full colour in the oxidized state, whereas, if $E = E_0 - 0.05$ volt, the colour will be nearly identical with that of the completely reduced form. Thus the colour change from one extreme to the other takes place over a potential range of about 0.1 volt. To obtain a sharp end-point, however, E_0 of the indicator should differ by at least 0.15 volt from those of the other systems involved, since an accurate estimate of the end-point is possible even in a potentiometric titration only if the standard potentials of the two systems, oxidant and reductant, differ by about 0.3 volt or more.

Further, it is apparent that an ideal indicator should not only satisfy the above condition but it should be strictly reversible, the two forms of it stable at high concentrations of acid, and the oxidized form highly resistant to irreversible oxidation at high potentials.

If the last condition were not satisfied, back titration of the excess oxidant becomes impossible and even in the forward titration, the indicator is partly destroyed in regions of local excess and the end-point rendered fleeting.

Judged on the above basis, with the exception of O-phenanthroline ferrous, no other available indicator could be regarded as ideal. Investigators in this field, therefore, were not merely concerned with introducing more indicators for use with the three oxidants referred to but also in developing ideal indicators which would meet all the requirements.

In the following pages are discussed some of the important indicators which have come into general use, and several others, which have been suggested but not well established, have been mentioned.

Diphenylamine, the first indicator of its kind, yields a marked colour change from bluish green to violet-blue at about 0.76 volt in acid solution. Since the S.O.P. of the ferric-ferrous system is 0.77 volt, it would appear at first sight that it could not be used in a ferrous-dichromate titration. The addition of fluoride or phosphate ions to the solution, however, reduces the concentration of the ferric ions and consequently the reducing potential of the ferric-ferrous system to well below 0.77 volt and thereby enables this indicator to be used. Though it could not be regarded as ideal in the strictest sense on account of its not being instantaneously reversible and its final colour being affected by excess of the oxidant, it has become established in ferrous-dichromate titrations.

With a view to evolve a better indicator, the effect of substituents has been investigated. Sarver and Kolthoff¹ first used diphenyl-amine-sulphonic acid and found that it gives a reddish-purple colour and its properties are similar to those of diphenylamine. The S.O.P. is somewhat higher (0.83 to 0.84 volt) than that of diphenylamine but is too low for many titrations including the very important one of ferrous ions with dichromate in the absence of phosphoric acid or fluoride.

Various other derivatives of diphenylamine have been synthesized and examined by Straka and Oesper², Walden and Edmonds⁴

and Cohen and Oesper³. Among these may be mentioned *p*-nitro- and 2:4-diamino-diphenylamine. The former has an oxidation potential about 0.2 volt higher than that of diphenylamine sulphonic acid and is somewhat more reversible. It yields an intensely reddish colour on oxidation and can be used for the direct titration of ferrous ions with ceric sulphate in the absence of phosphoric acid. It, however, suffers from the defect that it undergoes irreversible oxidation at high potentials and could not, therefore, be used for the back titration of excess ceric ions with ferrous sulphate. Further, it does not function well in a ferrous-dichromate titration on account of slow reaction. The latter indicator has a S.O.P. of 0.7 volt and is an excellent indicator with good reversibility, giving a red oxidation product which is not destroyed by an excess of dichromate and only slowly attacked by excess of ceric ions.

Besides its use in titrations with dichromate, diphenylamine has been recommended for ferrous-permanganate titrations in the presence of hydrochloric acid, stannic chloride and mercurous chloride by Scott⁵. It is claimed that any chlorine liberated does not escape but tends to oxidize the indicator thereby acting as so much permanganate. This, however, has been questioned by Manchot and Oberhauser⁶.

The indicator properties of the closely related diphenyl-benzidine and its sulphonic acid have been studied and it was found that the latter resembles diphenylamine sulphonic acid (Sarver and Fischer⁷). It yields a red colour in the oxidized state and is very useful in back titrations of dichromate with ferrous sulphate but at high concentrations of hydrochloric acid yields erratic results (Cohen and Oesper⁸). Irreversible oxidation yielding products of limited stability occurs at high potentials (Kolthoff⁸).

O-phenanthroline ferrous, 'ferroin' (Walden *et al.*⁹), is an indicator of a different type which is very suitable for use with ceric sulphate and satisfies all the conditions for an ideal indicator. The reduced and oxidized forms together form a reversible system with a S.O.P. of 1.14 volts, the former being intensely red in colour and the latter a feeble blue. This potential is high enough to give a correct end-point when substances with an oxidation potential

greater than 0.77 volt are titrated. The colour change is completely reversible and the oxidized form almost completely resistant to further oxidation. It is very useful in titrations of ferrous ions with dichromate, ceric sulphate or permanganate without the addition of fluoride or phosphoric acid. Though this indicator is superior to the diphenyl-benzidine indicators as regards stability and reversibility, it could not be regarded as a substitute to the latter since its S.O.P. is 0.3 to 0.4 volt higher. Thus there is still a need for indicators with oxidation-potentials between 0.7 to 1.1 volts (Kolthoff ⁸).

Other metallic complexes of O-phenanthroline have been investigated but no useful indicator has been found among them. The mono-nitro-derivative has a S.O.P. of 1.25 volts, is stable in acid solution and gives a sharp end-point from red to blue but when used with ceric sulphate and ferrous ions, the end-point is appreciably late (Hammett *et al.*¹⁰).

Various indicators analogous to diphenylamine have been proposed for titrations with dichromate. Among these may be mentioned naphthidine (Straka and Oesper ²), which is claimed to be superior to diphenylamine and diphenyl-benzidine, since the red colour of the oxidized form is in greater contrast to the green of the chromic ion than the violet-blue of the other two. In this connection it is of interest to note that brucine sulphate which has been used in ferrous-dichromate titrations yields a red colour at the end-point (D. S. N. Murty and T. R. Seshadri ¹¹).

A group of triphenylmethane dyes such as erioglaucine and eriogreen have been investigated (Knop ¹²). The oxidized forms of these indicators are generally of limited stability and undergo irreversible oxidation (Kolthoff ⁸). However, two indicators of this series, xylenecyanole F F and erioglaucine have been suggested for use with dilute permanganate and it is stated that the latter indicator renders the end-point with very dilute permanganate (0.005 N) more delicate.

A promising indicator which has been recently introduced is N-phenyl-anthranilic acid (O-diphenylamine carboxylic acid) (Syrokmsky and Stiepen ¹³). The S.O.P. of 1.08 volts is only slightly

less than that of 'ferroin' and it exhibits a delicate colour change from colourless to pink or pink-violet. The colour change is completely reversible, the oxidation product more stable than that from diphenylamine in presence of an oxidant and fading takes place only after several hours. It is particularly suitable for the determination of iron with dichromate, ceric sulphate or permanganate without adding fluorides or phosphoric acid.

Although there are now a large number of indicators for use with the common oxidants, very few are available for use with a reducing titrant such as titanous sulphate. The S.O.P. of the titanous-titanous system is about 0.05 volt and a useful indicator, therefore, should show a colour change at about 0.2 volt. Methylene blue which shows a colour change in acid solution at about 0.3 volt is the only reasonably satisfactory indicator now available (Glassstone¹⁴). A systematic investigation involving co-operation between analytical and organic chemists would no doubt lead to the discovery of other useful indicators.

In chemical analysis thorough testing and criticism are necessary and long periods of time frequently elapse before new reagents and procedures become established. It is equally true of these recently popularized investigations and in spite of the already large number of these indicators available, it is certain that many more would find application in analytical chemistry.

REFERENCES

- ¹ Sarver and Kolthoff, J. Am. Chem. Soc., 1931, **53**, 2902.
- ² Straka and Oesper, Ind. Eng. Chem., Anal. Ed., 1934, **6**, 465.
- ³ Cohen and Oesper, *ibid.*, 1936, **8**, 364.
- ⁴ Walden and Edmonds, Chem. Rev., 1935, **16**, 81.
- ⁵ Scott, J. Am. Chem. Soc., 1924, **46**, 1396.
- ⁶ Manchot and Oberhauser, Z. anorg. Chem., 1924, **138**, 189.
- ⁷ Sarver and Fischer, Ind. Eng. Chem., Anal. Ed., 1935, **7**, 271.
- ⁸ Kolthoff, *ibid.*, 1936, **8**, 237.
- ⁹ Walden *et al.*, J. Am. Chem. Soc., 1931, **53**, 3908.
- ¹⁰ Hammett *et al.*, *ibid.*, 1934, **56**, 1092.
- ¹¹ D. S. N. Murty and T. R. Seshadri, Proc. Ind. Acad. Sci., 1936, **3**, 38.
- ¹² Knop, Z. anal. Chem., 1931, **85**, 253.
- ¹³ Syrokonsky and Stiepen, J. Am. Chem. Soc., 1936, **58**, 928.
- ¹⁴ S. Glasstone, 'Oxidation-Reduction Potentials and their Applications'. Institute of Chemistry, (London), 1937.

A NEW APPROACH TO AN OLD PHENOMENON

By

G. V. L. N. MURTY

By his epoch-making discovery announced in the memorable year 1928, Sir C. V. Raman placed a new method at the disposal of the scientists, by the application of which it is in a way possible to make molecules write out their biographies on photographic plates. Of course, the writings of the molecules are not intelligible to the common man but they are not so to the scientist, who always develops and makes use of various types of uncommon sense, taking ample care to keep that of the common variety in tact. To the chemists as well as to the physicists, who have—more than many other things in common—immense inquisitiveness to acquire intimate knowledge regarding the affairs of molecules, the discovery came as a great boon. Thus studies of Raman spectra have yielded a new approach to many problems in physics and chemistry. Among the important applications of Raman effect to chemical problems the following may be mentioned:—

(1) Detection of the characteristic groups or linkages, which aids considerably in elucidating problems connected with molecular constitution, (2) detection of the presence of homocyclic or heterocyclic rings in molecules, (3) qualitative and quantitative analysis of mixtures of organic compounds, particularly terpenes, (4) detection of impurities, (5) study of isomerism, particularly of the keto-enol type, (6) influence of substituent groups on the bond strengths of organic compounds, (7) existence of isotopes, (8) structures of various inorganic acids and their salts, (9) phenomena of electrolytic dissociation and molecular association, (10) crystal structure studies, etc. This new method was found to be particularly useful to study the phenomenon of molecular association and hence it was employed by the author during his investigations.

It has been recognized long ago that molecules, which are generally supposed to be the ultimate particles of matter that are

capable of free existence, do not always remain as single units. They seem to be exhibiting a tendency to form groups or associated units. The concept of molecular association was first introduced by Henry¹ in 1878 and it has been attracting the attention of a considerable number of investigators ever since. By the term 'association' is meant the coalescence of a number of molecules with a degree of firmness that enables the group to act as a single unit during certain physical measurements. In the early days the term 'association' used to signify mainly the union between similar molecules, while that between dissimilar ones was frequently referred to as molecular complex (or compound) formation. Later work has shown that they are both inter-molecular co-ordination phenomena. However, it will be appropriate to specify them as homo and hetero molecular types of association respectively.

The abnormalities observed in various physical properties of a number of pure liquids were usually explained as due to the formation of aggregates of simple molecules to give an easily dissociated complex. Among the physical properties chiefly employed in this connection may be mentioned * (1) abnormal surface tension relationships, (2) abnormal critical ratios, (3) abnormal molecular weights in solution, (4) high latent heats of evaporation, (5) high dielectric constants, (6) the distribution ratios, and (7) the boiling points. The number of single molecules that constitute the complex was referred to as the association factor or the degree of association. The early work on the phenomenon of molecular association relates mostly to attempts at the determination of this degree of association. Almost all the methods employed depended upon the validity of formulae which are, in most cases, empirical. All those which obeyed the particular formula were considered normal and those which did not were abnormal, the abnormality serving to give a qualitative and sometimes a quantitative estimate of molecular association. The various methods employed for the determination of the degree of association have yielded in many

* Exhaustive references to the early work on 'association', classified according to the methods of study employed, are given in the thesis presented by the author to the Andhra University, 1940, pp. 22-23.

cases divergent values with the result that doubts were expressed by some (Longinescu and Chabroski ²) regarding the very existence of associated molecules. These authors proposed the theory of molecular accumulation or concentration to account for the behaviour of the so-called associated liquids. This concept takes into account a single molecule and not a complex one as the unit. The following table, containing the values of the degree of association of a few typical substances obtained by different methods, illustrates the widely varying nature of the results:—

Methods and the degree of association

Substance.	R.S.	R.R.I	B.	B.M.	W ₁ .	W ₂ .	D.M.	G.	L.
Water ..	2.66	1.405	1.10	..	1.98	2.57	1.96	1.82	4.6
Methyl alcohol ..	3.24	2.17	3.43	..	2.40	3.2
Ethyl alcohol ..	2.43	1.46	3.65	..	1.80	..	1.46	..	2.1
Formic acid ..	3.13	..	2.68	..	1.78	1.8
Acetic acid ..	2.9	1.79	2.74	..	1.95	1.7
n-Propylamine ..	1.24	1.20	1.5

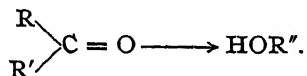
(R.S.—Ramsay and Shields; R.R.I.—Ramsay and Rose-Innes; B.—Batschinski; B.M.—Bennett and Mitchells; W₁—Walden's molecular cohesion method; W₂—Walden's application of Trouton's rule at the melting point; D.M.—Dutoit and Moijow; G.—Guye; L.—Longinescu.)

However, the recent results of electron diffraction investigations of Pauling and Brockway ³ have definitely proved the existence of aggregate molecules and have thus clearly shown that there is no need to doubt the existence of the phenomenon of homo molecular association.

The realization of the importance of the phenomenon of hetero molecular association dates back to the formulation of addition compounds as intermediate stages in all reactions by Kekule and Van't Hoff ⁴. The classical method for establishing the existence of compound formation in solution was introduced by Mendelejeff ⁵. It consists in plotting some physical property of a mixture against its concentration and noting the position of the discontinuities either in the curve itself or in some derived function. As examples of the physical properties usually employed may be mentioned density, viscosity, refractive index, magnetic rotation, compressibility, surface

tension, heat effects on mixing, electrical conductivity, light absorption, etc. The first attempt to deal with this problem in a quantitative manner was that of Dolezalek⁶. Vast amount of work was turned out in this field and a glance at the results shows that they are erratic and contradictory in nature*. A very satisfactory evidence for the existence of compounds in solution was obtained from freezing point measurements. Kendall and co-workers⁷ have made a series of studies of addition compound formation of organic substances by studying the curves relating to the melting point and composition of mixtures and their results gave very valuable information concerning molecular association of this type. They have thrown some light on the mechanism of association and have also shown its dependence on the chemical nature of the different molecular species.

The more recent work on the phenomenon of molecular association, making use of the X-ray and electron diffraction measurements and the investigations of infra-red absorption spectra, has clearly brought out the fact that the coalescence of molecules is not effected by any irregular assemblage but that it is governed by a definite mechanism satisfying the electronic concept of valency. It can be said that the hydroxylic compounds exhibit molecular association to a very great extent though the phenomenon is by no means confined to them. In recent years it is realized that association of the hydroxylic or amino compounds is caused by the tendency exhibited by the hydrogen atoms (of the $-OH$ or the $-NH_2$ groups) to serve as connecting bridges between two electronegative atoms. According to this concept the association between a carbonyl compound and an alcohol may be represented in general as:

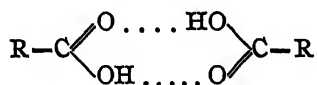


The arrow indicates the co-ordinate nature of the linkage joining the two molecules and it also shows that the carbonyl oxygen is the donor and the hydrogen of alcohol is the acceptor. Bonds

* A review of the early work is given by Washburn, vide Tech. Quarterly, 21, 399, 1908.

of this type are described as 'Hydrogen bonds'⁸ and they are sometimes denoted by dotted lines. It is now very well recognized that their formation is responsible for the association of hydroxylic compounds. This idea is amply supported by the vast amount of work turned out in recent years on the infra-red absorption spectra of liquids and liquid mixtures⁹.

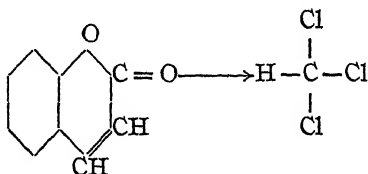
Among the early attempts at making use of the Raman effect for studying the phenomenon of molecular association may be mentioned the investigations of Rao¹⁰, Leitman and Ukhodin¹¹ and Meyer¹². Leitman and Ukhodin have noted the association of ethyl alcohol by an alteration in the shift of the $\Delta\nu_{623}$ line. Rao studied the Raman spectrum of water in great detail. The existence of a broad band with three distinct intensity maxima at $\Delta\nu_{3205}$, 3410 and 3582 cm^{-1} was attributed by him to the existence of the three types of molecules, viz. H_2O , $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ in equilibrium. An exhaustive investigation of the relative intensities of the three maxima in the Raman bands of water at different temperatures led Rao to postulate the predominance of the $(\text{H}_2\text{O})_3$ molecules in ice and the H_2O molecules in water at higher temperatures. From an investigation of the Raman spectra of carboxylic acids such as acetic, formic and benzoic acids Koteswaram¹³ has recently shown that they are associated in the free state and in solutions in non-polar solvents such as benzene and carbon tetrachloride. Following the representations of Pauling and Brockway³ the structure



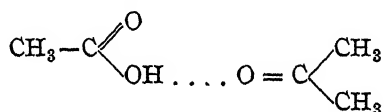
was given to the dimers (the dotted line representing the hydrogen bonds). It was also shown by the above investigator that the effect of rise of temperature and of dissolving in water was to shift the carbonyl frequency to longer wavelengths. This was explained to be due to a breaking up of the dimers to single molecules of the acid.

The changes observed in the Raman spectra of substances in solution were attributed by some previous workers to the formation of what are now called hetero molecular associates. Krishnamurti¹⁴

showed that acetic acid molecules get hydrated in aqueous solution and Parthasarathy¹⁵ observed that formic acid behaves similarly. Murty and Seshadri¹⁶ have shown that coumarin forms associates with chloroform by means of the following mechanism :

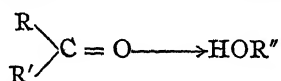


Koteswaram¹⁷ has recently pointed out that acetic acid and acetone exist as associates in mixture represented as:



The previous work seems to be more in the nature of explaining certain interesting results obtained in the investigations of the Raman effect by means of the phenomenon of molecular association. However, its importance can hardly be over-estimated because it has definitely established the efficacy of the Raman effect method to solve problems connected with molecular association.

The author has undertaken a systematic investigation of the 'hydrogen bonds' by means of the Raman effect. Since molecular association involving hydroxyl compounds is intimately connected with the formation of hydrogen bonds, the results of the investigations have provided certain amount of interesting information regarding the phenomenon of molecular association. The Raman spectra of a large number of carbonyl compounds containing the $C=O$ groups in different situations were studied in the pure state as well as in mixtures with some hydroxylic solvents. The formation of hydrogen bonds according to the mechanism



should result in a diminution of the strength of the $C=O$ linkage which may be expected to make itself manifest by causing a reduction of the $C=O$ frequency. This reduction was therefore taken as the

criterion for the formation of hydrogen bonds in the mixtures. The investigations have shown that hydrogen bonds are formed in many cases and that the reduction of the $C=O$ frequency is not the same in all of them. Obviously the $C=O$ bonds are weakened to different extents which means that hydrogen bonds of varying bond strengths are formed. The items of information that were so far considered to be of interest in connection with molecular association are the 'association factor' and the 'mechanism of association'. The present results have given rise to a new approach to the pretty old phenomenon of molecular association by making it possible to determine the strength of the hydrogen bond (or the strength of binding of the molecular associates). They have also succeeded in clearly bringing out the dependence of this factor on the chemical constitution of the molecules involved.

REFERENCES

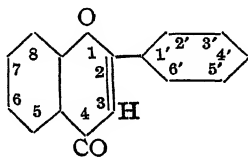
- ¹ Henry, *Annales de la Société Scientifique Bruxelles*, 1878, 3, 267.
Compt. rend. Association Francaise Pour l' advancement des sciences, 7 session, Paris, p. 409. 1878.
- ² Longinescu and Chabroski, *Chem. Rev.*, 1926, 6, 381.
- ³ Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1934, 20, 336.
- ⁴ Kekule, *Ann.*, 1858, 106, 140; Van't Hoff, 'Ansichten Über organische chemir' I, 225, 244, 1878.
- ⁵ Mendelejeff, *Z. Phys. Chem.*, 1878, 1, 273.
- ⁶ Dolezalek, *Z. Phys. Chem.*, 1908, 64, 724; Dolezalek and Schulze., *ibid.*, 1913.
- ⁷ Kendall *et al.*, *J. Amer. Chem. Soc.*, 36, 1222; *ibid.*, 36, 1722; *ibid.*, 36, 2498; *ibid.*, 37, 149; *ibid.*, 27, 1309; *ibid.*, 38, 1712.
- ⁸ Huggins, Undergraduate thesis, University of California, 1919; Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, 42, 1419.
- ⁹ Vide Murty, Thesis for the Ph.D. degree of the Andhra University, 1940, p. 19.
- ¹⁰ Rao, *Ind. J. Phys.*, 1928, 3, 123; *Nature*, 1930, 125, 600; *Proc. Roy. Soc.*, 1934, A145, 489.
- ¹¹ Leitman and Ukhodin, *J. Chem. Phys.*, 1934, 2, 825.
- ¹² Meyer, *Phys. Z.*, 1931, 32, 239.
- ¹³ Koteswaram, *Z. Physik.*, 1938, 110, 118; *ibid.*, 1939, 112, 404.
- ¹⁴ Krishnamurti, *Ind. J. Phys.*, 1931, 6, 367.
- ¹⁵ Parthasarathy, *Ind. J. Phys.*, 1931, 6, 287.
- ¹⁶ Murty and Seshadri, *Proc. Ind. Acad. Sci.*, 1938, 8, 519.
- ¹⁷ Koteswaram, Thesis, Madras University, 1939, p. 103, etc.

A NEW METHOD OF METHYLATING HYDROXY FLAVONES AND FLAVONOLS

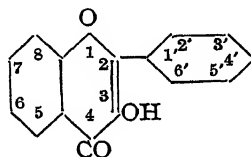
By

P. SURYAPRAKASA RAO

It is very well known that the hydroxyl group present in position 5 of hydroxy flavones and flavonols offers resistance to methylation, whatever might be the nature of the methylating agent used.

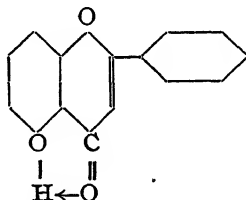


Flavone.



Flavonol.

The resistance is obviously due to the effect of chelation that exists between the carbonyl group in position 4 and the hydroxyl in position 5 as shown below:



Thus chrysin (5: 7-dihydroxyflavone)¹, apigenin (5: 7: 4'-trihydroxyflavone)², lotoflavin (a tetrahydroxyflavone)³, luteolin (5: 7: 3': 4'-tetrahydroxyflavone)⁴, scutellarein (5: 6: 7: 4'-tetrahydroxyflavone)⁵, quercetin (5: 7: 3': 4'-tetrahydroxyflavonol)⁶—all these are only partially methylated when treated with methyl iodide, the hydroxyl group in position 5 remaining unattacked. Diazomethane too does not produce complete methylation in several hydroxy flavones and flavonols, as, for instance, scutellarein⁵, herbacetin (5: 7: 8: 4'-tetrahydroxyflavonol)⁷ and gossypetin (5: 7: 8: 3': 4'-pentahydroxyflavonol)⁸.

However, using an excess of the reagent, Perkin could prepare the completely methylated (or ethylated in some cases) ethers of luteolin, quercetin and apigenin⁹, myricetin (5:7:3':4':5'-pentahydroxyflavonol)¹⁰, gossypetin¹¹ and quercetagetin (5:6:7:3':4'-pentahydroxyflavonol)¹². Hence he drew the conclusion that 'there was no difficulty in fully methylating compounds of this type, the failure in the past being due to the non-employment of an excess of the reagent'. In support of this conclusion, it was shown by Goldschmiedt and Zerner⁵ that scutellarein yielded the completely methylated ether also, when treated with excess of diazomethane. Quercetin too produced the pentamethyl ether, though to a small extent, under similar conditions¹³. A little later Herzig and Schönbach¹⁴ established the constitution of quercitrin, a glycoside of quercetin, by methylating all the free phenolic hydroxyl groups of the substance with diazomethane and identifying the partially methylated aglucone obtained as a result of the hydrolysis of the methylated glycoside. The same method was followed a few years ago by Attree and Perkin¹⁵ to settle the positions of the sugar nuclei in some glycosides of quercetin. The constitution of myricitrin has also been recently established by Hattori and Hayashi¹⁶ by adopting a similar procedure. It should be remembered that in all these cases there is a hydroxyl group in position 5 and it could be methylated successfully.

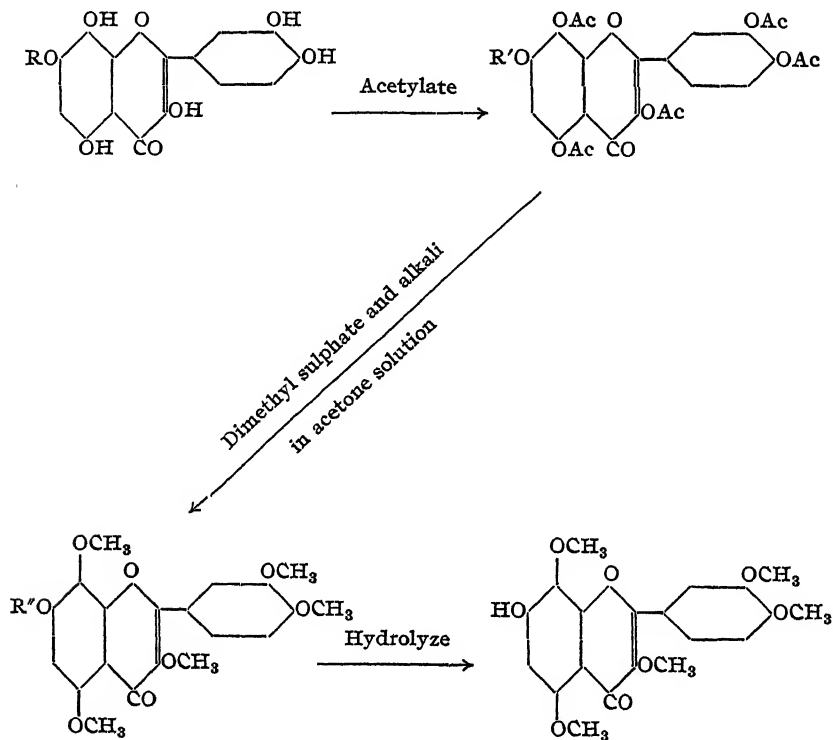
It is thus evident that complete methylation of hydroxy flavones and flavonols takes place in some cases, provided an excess of the reagent is used. It should, however, be noted that, though complete methylation was possible, the yield of the fully methylated compounds was poor indeed. Further the two processes of methylation, involving methyl iodide and diazomethane were too laborious and prolonged, extending over a number of days.

Besides methyl iodide and diazomethane, dimethyl sulphate in conjunction with alkali can be used for bringing about methylation of a phenolic hydroxyl group. The usual procedure for methylation with this reagent cannot be applied in the case of the hydroxy flavones and flavonols, since they are very readily oxidized in alkaline media. Hence several modifications^{17, 18, 19} have to be

adopted for a successful application of this reagent for methylation of these substances, and the most notable of these modifications is that of Cohn and Freudenberg²⁰ who tried to methylate quercetin by way of acetyl quercetin. Even this method did not produce the completely methylated ether as the sole product; the partially methylated compound also was invariably formed.

A new method has now been worked out to produce exclusively the fully methylated compounds in almost quantitative yields. The starting material is the acetyl derivative of the hydroxyflavone or -flavonol. In acetone solution, it is treated alternately with dimethyl sulphate and 20% alkali and the contents are made distinctly alkaline at the end. After leaving overnight, the excess of the methylating agent is destroyed and the solvent distilled off, when the methylated product usually separates out. If it does not, the contents should be made acidic, in which case the precipitation is immediate and almost complete. In this process the use of acetone as the solvent has produced the remarkable result that the completely methylated ethers are the exclusive products. Acetone seems to possess a specific influence in the methylation of the hydroxyl group in position 5 of the flavones and flavonols as was observed by Baker and Robinson²¹. During the course of the reaction the acetate seems to undergo deacetylation and simultaneous methylation, thereby preventing the decomposition of the free pigment through oxidation. All the phenolic groups are methylated smoothly without any exception. This method has been found to be very general and has been successfully employed to prepare the completely methylated ethers of gossypetin, herbacetin and quercetin²², quercetagetin²³ and the new flavonols 'cannabiscetin' and 'patuletin'²³ recently isolated in our laboratories. This new method has also been found to be a powerful tool in solving the thorny problem of establishing the constitutions of several glycosides. The substance is methylated through its acetyl derivative in acetone solution with dimethyl sulphate and alkali as described already, and the methylated glycoside on hydrolysis gives rise to an aglucone containing one free hydroxyl group in the nucleus and the position of the hydroxyl group determines the point of

attachment of the sugar residue in the glycoside. To represent the course of the general reaction, the transformations with gossypitrin, a glucoside of gossypetin may be produced diagrammatically as follows:



(R is sugar residue; R' is fully acetylated sugar residue; R'' is partially methylated sugar residue.)

By an application of this method it has been shown by the author that gossypitrin²⁴, herbacitrin and quercimeritrin²⁵ are 7-glucosides of gossypetin, herbacetin and quercetin respectively. The same procedure has also been employed to establish the constitutions of the new glucosides, 'quercetagitritin' and 'cannabiscitrin'²⁶. The remarkable feature about the last-mentioned glucoside is that it carries the sugar group in 3' position in the hydroxy phenyl nucleus. Till now only positions 3 and 7 are known to be involved in glycoside-formation and hence cannabiscitrin is the first glucoside of its kind to be isolated in the whole series of the flavones and the flavonols.

REFERENCES

- ¹ Kostanecki, Ber., 1893, 26, 2901.
- ² Perkin, J.C.S., 1897, 815.
- ³ Dunstan and Henry, Proc. Roy. Soc., 1901, 68, 374-78.
- ⁴ Perkin and Horsfall, J.C.S., 1900, 1314.
- ⁵ Goldschmiedt and Zerner, Monatsh, 1910, 31, 439-491.
- ⁶ Herzig, Monatsh, 5, 72.
- ⁷ Suryaprakasa Rao, Rangaswami and Seshadri, Proc. Ind. Acad. Sci., 1939, 9, 133.
- ⁸ Suryaprakasa Rao and Seshadri, Curr. Sci., 1939, 8, 256.
- ⁹ Perkin, Proc. Chem. Soc., 1912, 28, 329.
- ¹⁰ Perkin, J.C.S., 1902, 206.
- ¹¹ Perkin, J.C.S., 1913, 654.
- ¹² Perkin, J.C.S., 1913, 209.
- ¹³ Herzig, Monatsh, 1912, 33, 683-699.
- ¹⁴ Herzig and Schönbach, Monatsh, 1912, 33, 678.
- ¹⁵ Attree and Perkin, J.C.S., 1927, 234.
- ¹⁶ Hattori and Hayashi, Acta Phytochemi, 1931, 5, 213-218.
- ¹⁷ Wallashko, Br. Chem. Abs., 1904, 760.
- ¹⁸ Herzig and Hofmann, Ber., 1909, 42, 155.
- ¹⁹ Perkin and Watson, J.C.S., 1915, 107, 207.
- ²⁰ (a) Cohn and Freudenberg, Ann., 1923, 433, 230.
(b) Anderson, Canad. J. Res., 1932, 7, 283.
- ²¹ Baker and Robinson, J.C.S., 1928, 3117.
- ²² Suryaprakasa Rao and Seshadri, Curr. Sci., 1939, 8, 255.
- ²³ Unpublished work of the author.
- ²⁴ Suryaprakasa Rao and Seshadri, Proc. Ind. Acad. Sci., 1939, 9, 177.
- ²⁵ Suryaprakasa Rao and Seshadri, Proc. Ind. Acad. Sci., 1939, 9, 365.
- ²⁶ Unpublished work of the author.

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STUDY II OF DR. C. R. REDDY BY
MR. K. RAM MOHAN SASTRI.

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C. D. Reddy
24-8-1940.

Ram Mohan Sengupta —
Wastan
22nd Apr 1940.

THE RELATIONSHIP OF VITAMINS TO ENZYMES

By

K. V. GIRI

In recent years the relation of vitamins to enzyme systems has attracted considerable attention. The simultaneous expansion of knowledge in the field of enzymes and vitamins has not only elucidated the chemical nature of certain enzymes, but also has thrown considerable light on the physiological function of vitamins.

Certain vitamins are found to be the essential components of some enzymes which are concerned in the oxidation and reduction reactions of the cell. The vitamin or the molecule containing the vitamin is coupled with a protein carrier and the combination thus formed exhibits enzymic activity. In certain instances such vitamin-protein complexes constitute a member of a system which is necessary for the activation of important enzymes. The three vitamins which are known to exhibit such relationships to enzymes are the members of the B complex—vitamin B₁, vitamin B₂ and nicotinic acid (Pellagra-preventive factor).

It is interesting to know that many of the vitamins exist particularly in the animal tissues like liver and in yeast in bound form, combined with compounds of high molecular weight. Such bound forms of vitamins form the major portion as compared to the free vitamins. The bound forms of vitamins possess not only the biological function of vitamins but also they serve as indispensable catalytic systems in cell respirations. Euler has proposed the term '*Vitazymes*' for those vitamins which exert their function in the organism by combining with a colloidal bearer to form an enzyme. It is probable that the growth-promoting properties and other biological functions of vitamins are due to their being converted in the body, in combination with other substances into enzymes which function as important catalytic systems. The linkage between vitamins and enzyme systems will, therefore, prove to be of great

importance for the proper understanding of the metabolic function of vitamins in the living cell.

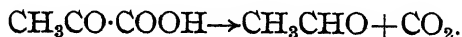
The writer hopes, in this article, to bring into focus the work done by him and others on the relationship between enzymes and vitamins and present in a concise form the present state of our knowledge in this field.

Vitamin B₁

As coenzyme in the oxidative breakdown of pyruvic acid.—The classical work of Peters and his associates at Oxford University has shown that vitamin B₁ functions as a coenzyme in the metabolism of carbohydrates, and particularly in the oxidative breakdown of pyruvic acid. It is well known that lactic acid is an intermediate metabolite in the biological oxidation of glucose, and the lactic acid in turn is oxidized to pyruvic acid by the action of the enzyme lactic acid dehydrogenase. Peters and his associates have shown that the brain of B₁ deficient pigeons exhibit lowered respiration in the presence of dextrose, and the addition of vitamin B₁ is found to restore it to normal condition. Further investigation showed that the brain of B₁ deficient pigeons when allowed to respire in presence of added lactate without vitamin B₁, an increase in pyruvate was observed, and which increase was reduced on the addition of vitamin B₁. Thus it is clear that vitamin B₁ in some way causes the disappearance of pyruvate.

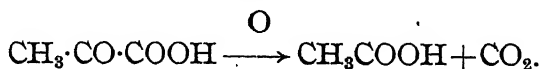
The mechanism of the breakdown of pyruvic acid as influenced by the addition of vitamin B₁ has been studied more intensely in recent years. Two mechanisms may be suggested for its breakdown :

1. Simple decarboxilation with formation of acetaldehyde and CO₂.



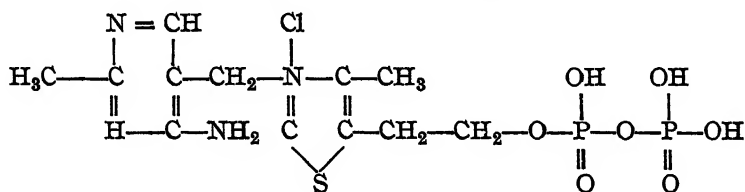
This is brought about by the action of an enzyme *carboxylase*.

2. Oxidation with the production of acetic acid and CO₂.



This change is brought about by *pyruvic acid oxidase*.

Carboxylase is an enzyme which is responsible for promoting the anaerobic breakdown of pyruvic acid in mammalian tissues. This is one of the components of enzymes of the zymase complex of yeast. It requires for its activity a coenzyme, which is known as cocarboxylase (Auhagen, 1932). In the year 1937 Lohmann and Schuster (1937) working in Meyerhof's laboratory isolated cocarboxylase from yeast in crystalline form and it was found to be a pyrophosphoric ester of vitamin B₁. The formula of this compound as suggested by Lohmann and Schuster is given below:



Formula of cocarboxylase according to Lohmann

This discovery by Lohmann led many workers to synthesize cocarboxylase from vitamin B₁. Stern and Hofer (1937) synthesized it *in vitro* from synthetic vitamin B₁ and POCl₃. Tauber (1938) obtained it from sodium pyrophosphate, orthophosphoric acid and vitamin B₁. Several workers have prepared cocarboxylase by enzymic synthesis. Euler and Vestin (1937), Tauber (1937), and Peters (1937) obtained cocarboxylase by enzymic synthesis, with rat liver, with acetone-dried preparations from pig's duodenal mucosa, and with avitaminous brain brei respectively. Tauber's claim that acetone-dried preparations of duodenal mucosa from the pig can synthesize cocarboxylase has been recently refuted by Ochoa (1939) who showed that preparations from duodenal mucosa (pig) showed no activity under various experimental conditions, while liver from avitaminous pigeons possesses higher synthetic activity as compared with that of brain and muscle. The synthetic action observed by Tauber is attributed to the growing bacteria in the medium.

Whether the first mechanism, namely, the decarboxilation of pyruvic acid occurs to a large extent in animal metabolism is a doubtful

one, although this is common in plant metabolism. The second mechanism, namely, oxidation with the production of acetic acid and CO_2 has been suggested to be more probable in animal metabolism. If vitamin B_1 assists this reaction also, then it acts as a *Co-oxidase* or coenzyme in the oxidation of pyruvic acid. It was reported by Lipmann (1937) that such an action is exerted by Lohmann's pure cocarboxylase (vitamin B_1 pyrophosphate). He showed that the respiration of alkaline washed *Bacterium Delbrückii* with pyruvate as the substrate is increased by cocarboxylase, the reaction products being acetic acid and CO_2 . Recently an interesting case has been reported by Lipmann (1939) in which vitamin B_1 pyrophosphate acts as a link of the reaction-coupling of oxidation-reduction and phosphorylation. He has shown that coupling between pyruvic acid dehydrogenation and adenylic acid phosphorylation takes place with vitamin B_1 pyrophosphate as a link of the reaction with dry preparations of *Bacterium Delbrückii*. Vitamin B_1 pyrophosphate is the prosthetic group of the enzyme catalyzing the dehydrogenation of pyruvic acid. The relation between vitamin B_1 and adenylic acid system is of considerable importance from the point of view of the function of vitamin B_1 in the living cell.

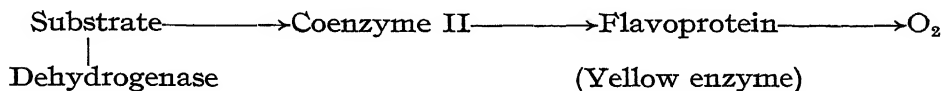
It is, therefore, clear from the foregoing that vitamin B_1 owes its biological action in part at least to its function as a coenzyme after phosphorylation in tissues, assisting either the pyruvic acid carboxylase or its oxidase in breaking down the pyruvic acid. The vitamin also exerts important function in the oxidative phosphorylation of adenylic acid.

Vitamin B₂

(Synonymous with riboflavin, lactoflavin, and vitamin G)

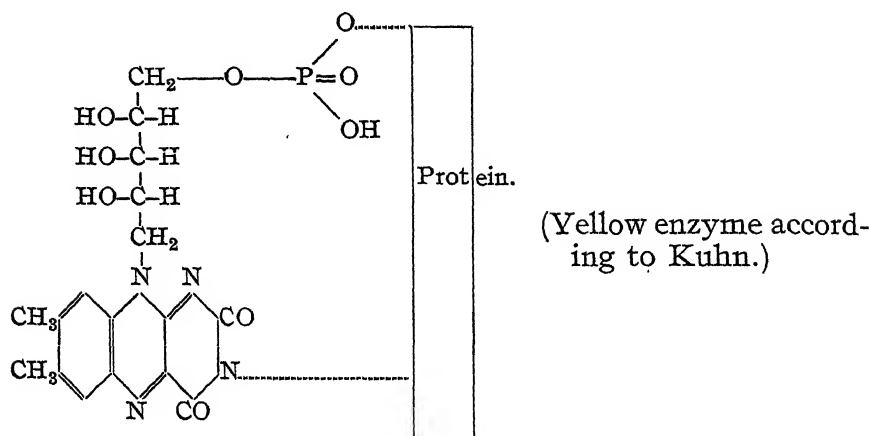
Flavin is a very important and widely distributed natural pigment. Our knowledge of the action of this pigment in cell respiration is mainly due to the work of Warburg and Christian (1932, '33), who showed that it can act as respiratory carrier when combined with a protein, as flavoprotein. The protein has been isolated and its action studied in various oxidation-reduction systems.

This flavoprotein is otherwise known as '*Yellow enzyme*'. It was isolated from yeast. It is reduced by dehydrogenase systems and in turn spontaneously reoxidized by oxygen, in the same way as methylene blue or other reduced dyes. But the reduction of the pigment by dehydrogenase system is not direct, as another intermediary link is necessary to bring about the reaction between the activated substrate and the flavoprotein. The typical system in which flavoprotein acts as carrier may be represented as follows:



The substrate, hexosemonophosphoric acid, is activated by an enzyme, dehydrogenase, and is oxidized by coenzyme II, but not by flavoprotein or by oxygen. The reduced coenzyme is reoxidized by flavoprotein, which is further oxidized by O_2 . Thus in this system the transfer of hydrogen follows the sequence indicated.

The yellow enzyme is the first instance of the separation and identification of the prosthetic or chemically active group of an enzyme. This enzyme has been isolated in crystalline form by Theorell (1934). The separation of the two components of this enzyme—the protein and riboflavin—has been accomplished by dialysis, neither of which act as carriers of oxygen. On combination, however, they can function as an enzyme. The protein fraction of the enzyme cannot be replaced by other proteins. The prosthetic group of the yellow enzyme is found to be the flavin phosphate. The connecting link between the riboflavin and the protein component of the enzyme is the phosphoric acid radical. Kuhn (1936) suggested that the protein component of the enzyme is bound to the phosphoric acid radical and to the free imide group in position 3 of the riboflavin-5-phosphoric acid. The combination of the protein and riboflavin phosphoric acid ester is represented as follows:



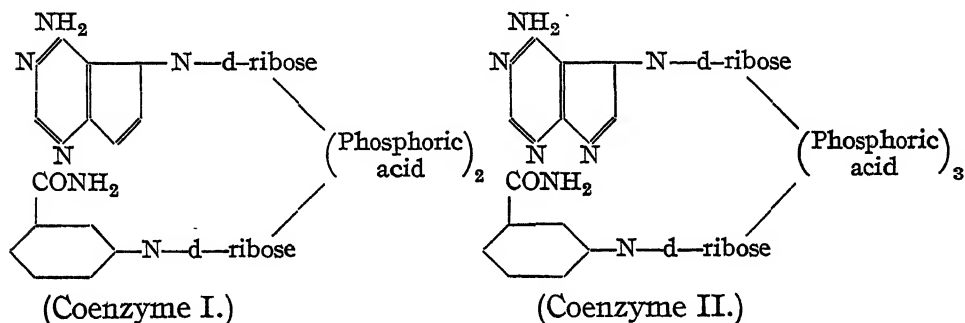
Riboflavin as the prosthetic group of other enzymes.—In addition to the yellow enzyme, a riboflavin-protein, a number of flavoproteins have been isolated, which have as their prosthetic group riboflavin and adenylic acid. This is called according to Warburg alloxazine-adenine-dinucleotide. The coenzyme of d-alanine oxidase, isolated from horse kidney, was found to be a flavin dinucleotide (Warburg and Christian, 1938). Xanthine oxidase is shown to be an alloxazine proteid (Balls, 1938). Straub (1939) has recently isolated another flavoprotein from heart muscle tissue, which has flavin-adenine dinucleotide as its prosthetic group. This flavoprotein was subsequently found to be identical with diaphorase or coenzyme factor (Corran, Green and Straub, 1939), which is a special catalyst for the oxidation of reduced coenzyme I or II. Another flavoprotein has been isolated recently, which has the property of catalyzing specifically the oxidation of aldehydes to their corresponding acids (Subrahmanyam and Green, 1939; Gordon, Green and Subrahmanyam, 1940). The prosthetic group of this enzyme is found to be flavin adenine dinucleotide. Thus the importance of riboflavin in the synthesis of the prosthetic group of several enzymes is indicated by the examples given above, and there may be many more enzyme systems, in which riboflavin constitutes the prosthetic group.

Nicotinic Acid (Pellagra-preventive factor)

Nicotinic acid amide as coenzyme.—The discovery that nicotinic acid or its amide is a vitamin whose deficiency is responsible for

pellagra has stimulated much interest because the pyridine ring which it contains is found to play an important rôle in cellular respiration. It is now well recognized largely through the work of Warburg and Euler that nicotinic acid amide is a constituent of both coenzyme I (Diphosphopyridine-nucleotide designated Co I) and coenzyme II (Triphosphopyridine-nucleotide designated Co II), which play important rôle in respiration and metabolic processes in the body. Coenzyme I contains one molecule of nicotinic acid amide, two of phosphoric acid, two of pentose and one of adenine, while the coenzyme II contains all the above-mentioned constituents with one more molecule of phosphoric acid.

The constitution of the two coenzymes are presented below:



The coenzyme is reduced by the substrate in presence of suitable dehydrogenase and again oxidized indirectly by molecular oxygen. Thus it acts as a carrier of hydrogen in biological oxidations. This cycle of oxidation occurs in the pyridine ring. Therefore the mechanism of the oxidation and reduction is the same in both coenzymes. But each coenzyme is specific for a particular type of dehydrogenase. This coenzyme specificity of the dehydrogenases is an interesting problem in enzyme chemistry, which requires further elucidation.

The two coenzymes are distributed in all the tissues of the body, and therefore it would be of interest to know whether there exists any relation between the dietary intake of nicotinic acid and the coenzyme content of tissues and blood. The concentration of coenzyme in the blood is sensitive to the ingestion of nicotinic acid both in normal individuals and pellagrins. It is also reported

(Axelrod and Elvehjem, 1939) that the coenzyme content of the tissues of normal animals (dogs and pigs) remain constant, while in nicotinic acid deficiency there is a definite decrease in the coenzyme content of liver and muscle. These findings, together with the fact that the deficiency of nicotinic acid causes pellagra, lead to the conclusion that the coenzyme level of the body will be reduced in pellagra, thereby reducing the capacity for oxidation-reduction processes in the body. It is doubtful, however, whether the coenzyme rôle of nicotinic acid can explain all of the facts relating to pellagra.

Vitamin B₆

Vitamin B₆ is another member of the B vitamins, which prevents or cures an acrodynia like dermatitis in young rats. The structure of the vitamin has been established, and its synthesis also reported. It is a derivative of the nitrogenous base pyridine, being a methyl-hydroxy-dihydroxymethyl substituted pyridine. Thus the importance of pyridine nucleus, already established in the case of nicotinic acid and its amide in biological oxidations and reductions, appears to indicate that certain functions of vitamin B₆ may be related to similar types of biological reactions. But so far no evidence is forthcoming in this direction.

Vitamin C

Activation and inhibition of enzymes by vitamin C.—The activities of several enzymes are known to be markedly influenced by vitamin C. Enzymes may be divided according to their behaviour towards vitamin C into two groups.

Group I: Enzymes activated by vitamin C either in presence or absence of metallic catalysts. Papain, Cathepsin (Purr, 1933; Euler *et al.*) and arginase (Purr, 1933; Edlbacher and Leuthardt, 1933; Karrer and Zehender, 1934) belong to this group.

Group II: Enzymes which are inhibited by vitamin C either in presence or absence of metallic catalysts. Catalase (Euler and Larsson, 1934; Euler, Karrer and Zehender, 1934), invertase (Weidenhagen and Dal-Chueng, 1936), amylase (Purr, 1934; Hanes, 1935;

Euler, Karrer and Zehender, 1934; Weidenhagen and Dal-Cheung, 1936) and phosphatase (Giri, 1937*a, b*, 1938 and 1939).

The relation between vitamin C and phosphatases has engaged the attention of the author in a detailed experimental enquiry on the rôle of phosphatases in plant and animal life. Beginning with the study of plant phosphatases the author established a relationship between vitamin C oxidation and the inhibition of the activity of the phosphatase. The oxidation of vitamin C by metallic catalysts like Cu^{\bullet} and oxidizing agents is found to inhibit the activity of the enzyme. Neither vitamin C nor Cu^{\bullet} alone has any effect on its activity, under the experimental conditions used. The inhibition by vitamin C-Cu complex is entirely annulled by glutathione (GSH), cysteine, Cystine, H_2S and reducing agents like potassium cyanide and sodium hydrosulphite. The hydrolysis of pyrophosphate by the enzyme is less affected by vitamin C-Cu complex than that of glycerophosphate. This difference in the behaviour of pyrophosphate and glycerophosphate hydrolysis towards the complex is attributed to the protective action exerted by pyrophosphate on the vitamin against catalytic oxidation (Giri, 1937*b*). Dehydroascorbic acid either alone or in presence of Cu^{\bullet} is found to have no influence on the activity of the enzyme. The author's findings on plant phosphatases have been recently confirmed and extended, by Courtois and Manouerier (1939) in Paris, to the hydrolysis of various types of phosphoric esters, and similar results were obtained. The study was later extended to animal enzymes (Giri, 1939). Similar to plant phosphatases, the activities of the alkaline and acid phosphatases of kidney, liver and brain are inhibited by the vitamin C-Cu complex, and the inhibition is found to be entirely or partly annulled by glutathione and other sulfhydryl compounds and reducing agents. The activity of the phosphatase present in the crude aqueous extracts of tissues, with the exception of that of brain, is not influenced by the complex, while the activity of the purified extracts is inhibited by vitamin C-Cu complex. This difference in behaviour of the extracts is due to the presence of certain factors in crude extracts which protect the vitamin against oxidation. The isolation and nature of the protective mechanism existing in animal tissues has

been investigated, and it is found that the protective mechanism is mainly confined to the colloidal constituents of the tissue extracts (Giri and Shourie, 1940). It is clear, therefore, that the oxidation of vitamin C induces the inhibition of the activity of phosphatases, and factors which prevent the oxidation of the vitamin will protect the activity of the enzyme from inhibition by vitamin C-Cu complex.

In view of the above it is understandable that vitamin C, Cu⁺⁺ and protective substances, which occur together in all tissues, play an important rôle in the regulation of the activity of phosphatases.

Another important function of vitamin C in its relation to enzymes is that it protects enzymes (phosphatase, amylase, and pepsin) from destruction by ultra-violet radiation (Giri, 1941).

Vitamin C as coenzyme.—A very interesting example of hydrogen transport by vitamin C was given by Hopkins and Morgan (1936). They showed that glutathione protects vitamin C against oxidation by ascorbic acid oxidase. The mechanism of this protection has been explained as being due to the fact that the oxidized vitamin reacts with glutathione with reformation of reduced vitamin and production of oxidized glutathione, this reaction being much faster than the oxidation of vitamin C. In this case vitamin C acts as a coenzyme for the glutathione oxidation.

It will be seen from the foregoing that vitamins are indispensable for the activity of certain enzyme systems in the body. The vitamin requirement of the body is, therefore, of supreme importance, as they play essential rôle in the oxidation and reduction processes, which promote the life of the cell. We are still a long way from being able to link up studies of the physiological rôle of other vitamins with studies of the action of enzyme systems in the body. It is clear that ordered knowledge of their relationship will assist greatly in our understanding of the intimate mechanisms of many vital activities of which those mentioned above are only a fraction, and will bring us distinctly nearer to an understanding of the fundamental processes in living matter.

REFERENCES

- ¹ Auhagen (1932), *Z. Physiol. Chem.*, **204**, 149; **209**, 20; *Biochem. Z.*, **258**, 330 (1933).
- ² Auhagen, A. E. and Elvehjem, C. A. (1939), *Nature, Lond.*, **143**, 281.

- ³ Balls, E. G. (1938), *Science*, **88**, 131.
- ⁴ Corran, H. S., Green, D. E. and Straub, F. B. (1939), *Biochem. J.*, **33**, 793.
- ⁵ Courtois, J. and Manouerier, J. (1939), *Compt. rend. soc. de. Biol.*, **131**, 157; *Enzymologia*, **6**, 342.
- ⁶ Edlbacher, S. and Leuthardt (1933), *Klin. Wochschr.*, **12**, 1843.
- ⁷ Euler, H. V., Karrer, P. and Zehender (1934), *Helv. Chim. Acta.*, **17**, 157.
- ⁸ Euler, H. V., Larsson, H. (1934), *Arkiv. kemi. mineral geol.*, **11A**, **7**, No. 3.
- ⁹ Euler, H. V. and Vestin, R. (1937), *Naturwissenschaften*, **25**, 416.
- ¹⁰ Giri, K. V. (1937a), *Z. Physiol. Chem.*, **245**, 185.
- ¹¹ Giri, K. V. (1937b), *Ind. J. Medical Research*, **25**, 443.
- ¹² Giri, K. V. (1938a), *Nature, Lond.*, **141**, 119.
- ¹³ Giri, K. V. (1938b), *Z. Physiol. Chem.*, **254**, 126.
- ¹⁴ Giri, K. V. (1939), *Biochemical J.*, **33**, 309.
- ¹⁵ Giri, K. V. (1941), *J. Ind. Chem. Soc.*, **18**, 141.
- ¹⁶ Giri, K. V. and Shourie, K. L. (1940), *Ind. J. Medical Research*, **27**, 685.
- ¹⁷ Gordon, A. H., Green, D. E. and Subrahmanyam, V. (1940), *Biochem. J.*, **34**, 764.
- ¹⁸ Hanes, C. S. (1935), *Biochem. J.*, **29**, 2588.
- ¹⁹ Hopkins and Morgan (1936), *Biochem. J.*, **30**, 1446.
- ²⁰ Karrer, P. and Zehender, P. (1934), *Helv. Chim. Acta.*, **17**, 737.
- ²¹ Kuhn, R. and Rudy, H. (1936), *Ber.*, **69**, 1974.
- ²² Lipmann, F. (1937), *Nature, Lond.*, **140**, 25; *Enzymologia*, **4**, 65.
- ²³ Lipmann, F. (1939), *Nature, Lond.*, **143**, 281.
- ²⁴ Lohmann, K. and Schuster, P. (1937), *Naturwissenschaften*, **25**, 26.
- ²⁵ Lohmann, K. and Schuster, P. (1937), *Biochem. Z.*, **294**, 188.
- ²⁶ Lohmann, K. (1937), *Z. f. angew. Chem.*, **50**, 232.
- ²⁷ Ochoa, S. (1939), *Biochem. J.*, **33**, 1262.
- ²⁸ Peters, R. A. (1937), *Biochem. J.*, **31**, 2240.
- ²⁹ Purr, A. (1933), *Biochem. J.*, **27**, 1703.
- ³⁰ Purr, A. (1934), *Biochem. J.*, **28**, 1141.
- ³¹ Straub, F. B. (1939), *Biochem. J.*, **33**, 787.
- ³² Stern, K. G. and Hofer, J. W. (1937), *Enzymologia* (Neuberg-festschrift), **3**, 82.
- ³³ Subrahmanyam, V. and Green, D. E. (1939), *Nature, Lond.*, **144**, 1016.
- ³⁴ Tauber, H. (1937), *Science*, **86**, 180.
- ³⁵ Tauber, H. (1938), *J. Amer. Chem. Soc.*, **60**, 730.
- ³⁶ Theorell, H. (1934), *Biochem. Z.*, **272**, 155; **275**, 37.
- ³⁷ Warburg, O. and Christian, W. (1932), *Biochem. Z.*, **254**, 438.
- ³⁸ Warburg, O. and Christian, W. (1933), *Biochem. Z.*, **266**, 377.
- ³⁹ Warburg, O. and Christian, W. (1932), *Naturwissenschaften*, **20**, 980.
- ⁴⁰ Warburg, O. and Christian, W. (1938), *Biochem. Z.*, **196**, 294; **298**, 150.
- ⁴¹ Weidenhagen, R. and Dal-Cheung (1936), *Z. Wirtschaftsgruppe Zuckerind.*, **86**, 240, 438.

IMPORTANT CITRUS FRUITS OF THE CIRCARS

QUALITY OF THEIR JUICES AND THEIR PRESERVATION

By

C. J. DASA RAO

As a class the Citrus plants belong to a genus of shrubs or trees usually spinous and come under the natural order Rutaceae. The citrus family has such a large number of species and varieties that it is very difficult to classify them. The following seems to be a reasonable classification. *Citrus aurantium*, Linn; the *Citrus medica*, Linn; and the *Citrus decumana*, Linn. Each species has a number of varieties. They can be distinguished by the size of the fruits, the taste of the juices and the medicinal properties. The following are the important citrus fruits available in plenty in the Andhradesa and they can be allotted to the various botanical species. The Kamalas and the Batavias are medium sized fruits and belong to the species *citrus aurantium*. The Narinja, the Dabba, the Lemon and the Lime are smaller sized fruits and belong to the species *citrus medica*. The Matheepala, the Indian Shaddock and the Grape fruit are the biggest sized fruits and belong to the species *citrus decumana*. Most of the varieties above mentioned are indigenous to India, except the batavias and the grape fruit.

The citrus trees grow very well in plains and up to a height of 6,000 feet above sea-level. They require a well-drained or rich loamy soil with a moderate supply of water and rainfall. A good number of varieties of citrus trees thrive very well in Andhradesa because it has a good soil and gets moderate rainfall. Godavari, Krishna, Guntur, Vizagapatam and Chittor districts produce a large quantity of citrus fruits. A good portion of these fruits does not find markets for want of suitable organizations and export facilities. Thus a large quantity of these citrus fruits go to waste and any method of disposing them off and enriching the growers will be a sound utilization of the waste.

A brief description of the available fruits and their medicinal properties are given below:

Citrus aurantium, Linn.: *Variety 1.*—The Kamalas. The fruits are orange coloured, round and medium in size. The rind is thick and either adhering to the pulp or loose. The juice is sweet and slightly sour. It is a good tonic to the liver and a laxative. It is cooling and relieves vomiting. It is highly antiscorbutic.

Variety 2.—The Batavias. The fruits are bigger than the Kamalas with a yellow or a greenish yellow rind. The rind is either thick or thin, rough or smooth. The juice of the thin skinned variety is sweeter than that of the thick skinned variety. In general the juice is sweet and sour. It is highly antiscorbutic and valuable in bilious affections. It is a general tonic and improves the appetite. It can be used as the safest acid fruit.

The rind of both the above varieties possesses stomachic and tonic properties. The peels are useful as a carminative and for destroying intestinal worms.

Citrus medica, Linn.: *Variety 1.*—The Narinja. The fruits are medium shaped with a rough outer rind. They are greenish to yellow in colour. The rind is fairly thick with a white fleshy portion inside. The juice is usually sour though some varieties are sweet. It is a tonic and has stomachic properties. It is useful in bilious affections.

Variety 2.—The Dabba. The fruits are large and oblong with a rough furrowed and thick rind. The juice is sour and can be used as a tonic. It is a good refrigerant. The rind is used in confectionery.

Variety 3.—The Lemon. The fruits are small in size and round or oblong in shape. The rind is yellow and smooth. It is thin with a white fleshy portion inside. The juice is sour and antiscorbutic. In febrile and inflammatory affections, the diluted and sweetened juice forms an excellent refrigerant. It is also useful as an antidote for some acro-norctic poisons.

Variety 4.—The Limes. The fruits are the smallest among the citrus fruits. They are round or slightly oblong, with a yellow and thin rind. The juice is sour and sharp in taste. It is a good

appetizer, stomachic and anthelmintic. It cures abdominal complaints and removes constipation and fatigue. It is good for biliousness and relieves vomiting.

Citrus decumana, Linn.: *Variety 1*.—The Matheepala. The fruits are large and oval shaped. The outer rind is thick and rough. The inner portion is white and spongy. The juice is sour and bitter. It is highly nutritive and refrigerant. It allays hysterical palpitations of the heart and cures cough.

Variety 2.—The Indian Shaddock. The fruits are the largest among the citrus fruits. They are round or slightly oval with a thick greenish yellow rind. The inside of the rind has a thick spongy portion. There are two varieties, the white and the red ones. The juice is sweet and slightly bitter due to the very bitter rag surrounding the pulp. The juice is considered to be a tonic. It is nutritive and refrigerant.

Variety 3.—The Grape fruit. The fruits are large and round with a rough thin rind. The fruits are juicy. The juice is sour and bitter. Many like the taste of this fruit. It is of high medicinal value. It is a tonic and is used for complaints of the liver and for dyspepsia.

In spite of the great importance of the citrus fruits very little work was done in India in regard to their chemistry and the manufacture of fruit products. We have to depend mostly on data collected regarding the fruits available in America and elsewhere. Work was therefore initiated in the chemical laboratories of the Andhra University by Prof. Seshadri on the chemical study and utilization of Indian fruits and at the first stage the citrus fruits have been examined during the past three years. Some of the results have been embodied in the form of thesis submitted to the University and some publications in the Proceedings of the Indian Academy of Sciences. Meanwhile some work has been published from Lyallpur on the utilization of citrus fruits of the Punjab.

A detailed analysis has been carried out on the samples of juices obtained from all the varieties of citrus fruits available and a consolidated statement of these results is given below. Healthy and ripe fruits were procured from various parts of Andhradesa

and these were used for the experiments. These fruits were cut into halves and the juice gently squeezed out by using a motor driver squeezer. The seeds were separated and the juice passed through a felt filter bag to remove as much of the coarser suspended particles as possible. The clear juice was examined for the various components according to the official and tentative methods of analysis of the Association of Official Agricultural Chemists. The vitamin C content was determined by making use of the standard oxidation-reduction indicator 2-6-dichlor phenolindophenol.

The following table represents the average figures of a number of analysis of the different varieties of fruits carried out in these laboratories:—

	Citrus aurantium or sweet group.		Citrus medica or sour group.				Citrus decumana or bitter group.		
	Bata- vias.	Kama- las.	Na- rinja.	Dab- ba.	Le- mon.	Lime.	Shad- dock.	Grape fruit.	Ma- thee- pala.
Juice % Fruit ..	45.6	48.3	46.2	39.9	41.4	54.3	38.7	36.0	36.8
Acidity as citric acid ..	0.85	0.63	3.0	7.4	7.1	6.5	1.0	4.1	6.9
Sucrose ..	4.6	3.8	1.2	3.7	0.6	..
Reducing sugar ..	3.1	3.5	3.8	1.46	1.80	1.7	3.4	3.0	2.3
Total sugars ..	7.7	7.3	5.0	1.46	1.80	1.7	7.1	3.6	2.3
Total solids ..	10.2	10.1	9.8	9.3	9.4	9.3	9.6	9.7	9.3
Ash ..	0.54	0.52	0.47	0.43	0.44	0.28	0.48	0.32	0.45
Vitamin C (mg. per 100 g. of the juice) ..	48	43	44	28	31	40	38	31	36

The above results clearly indicate that the composition of the juices are different from species to species. The fruits belonging to the species *aurantium* have sweet juice with high sucrose and glucose content. The acidity of the juices is very small. They are also rich in vitamin C content. The fruits belonging to the species *medica* have sour juices. The juices generally do not contain any sucrose but contain a small quantity of glucose. They also contain vitamin C to an appreciable amount. The fruits belonging to the species *decumana* have generally sour and bitter juices except shaddock whose juice is sweet and bitter. The juices contain small

quantities of sucrose and glucose with low acid. They also contain vitamin C to an appreciable amount.

Preservation of Juice.—Taking the analytical data into consideration experiments were conducted to find out the best conditions for preservation of the juices. There are various methods of preserving citrus juices. Out of these only three methods are largely followed in most of the countries where citrus juices are preserved. In two of the methods chemicals like sodium benzoate and sulphur dioxide are used. The third and the most general method is based on the simple flash pasturization and vacuum sealing principle. Juice preserved by using sodium benzoate is found to give a chemical taste and odour. Juices preserved by the other methods are found to keep well and have an agreeable taste and flavour. But the aim of these investigations was to evolve a simple and cheap method for the preservation of citrus juices. Hence the experiments were confined to preserving juices by the flash pasturization method. In this method the raw juices are mixed up with varying quantities of sugar with or without the addition of citric acid depending upon the acidity of the juices. The made-up juices are flash pasturized at 200–205°F. for a few minutes, filled into previously sterilized bottles and vacuum sealed. Detailed experiments were carried out on the juices available to find out the optimum conditions for cheap and successful preservation. From the analytical figures given above the total solids content of the citrus juices is about 9–10% and the acid expressed as citric acid is about 0.6–7.5%. Hence varying quantities of sugar were added to bring the total solids content of the juices to 20, 25, 30, 35, 40, 45, 50, and 60%. Also the acidity of the made-up juices were kept from 1 to 4% by adding citric acid if required. It was found that juices containing 35% and above of total solids and an acidity above 2% preserve well over long periods. However it was found that juices (bitter) from grape fruit and matheepala taste better if preserved with 3.5 to 4% acidity and the rest of the juices with 2 to 2.5% acidity. From the above results a cheap and successful formula to preserve different juices on a commercial scale has been worked out as given below. For all juices the ratio of total solids in the preserved juice

to the total solids of the raw juice should be kept at 4 to 1 with the acidities given above. The juices preserved by this method when diluted four times their volume will give the consistency of the original juice and an acidity agreeable to taste.

The following is a brief description of the method adopted for the preservation of the various juices. Healthy and ripe fruits were selected and cut into halves. The juice was pressed out in a power driven squeezer. Immediately it was passed through a felt filter bag to remove coarse and suspended impurities. A sample of the juice was analyzed for total solids content and acidity expressed as citric acid. The total solids of the respective juices was made up to four times the total solids content of the raw juices by the addition of calculated amounts of sugar. If A is the total solids content of sugar (100), B the total solids content of the finished juice, and C the total solids content of the raw juice, then $(A-B)$ gives the parts of juice to be added to $(B-C)$ parts of sugar to obtain $(A-C)$ parts of finished juice of the desired total solids content. The acidity of the finished juices was increased to the desired level by the addition of pure citric acid to the raw juices or water as the case may be. The made-up juices were slightly heated to dissolve the sugar and then filled into recently sterilized crown cork bottles leaving a small space at the top for expansion of the juice during pasturization. The bottles were kept in a pressure cooker containing boiling water and the lid was closed. The bottles with the juices were kept inside the cooker for five minutes at 200–205°F. Then the bottles were removed from the cooker and sealed with sterilized caps with a sealing machine. The bottles were labelled and stored. Indian Shaddock could not be preserved well because a water soluble bitter compound naringin found in the rags came into the crushed juice and the preserved juice became more bitter.

A statement showing the recipes and the cost of manufacture is given in the tables below. The crown cork bottles used in these experiments were purchased at a cost of Rs.24 per gross. The costs of fruits are the averages for the whole season at Waltair. The costs of fruits are slightly higher at Waltair because fruits are imported from places where they are actually grown.

Name of fruit.	No. of fruits used.	Wt. of juice in Kg.	Bx. of juice.	Acidity of juice.	Bx. of final product.	Acidity of final product.	Wt. of sugars added in Kg.	Wt. of citric acid added.	Wt. of water added.
Batavias ..	200	15.5	10.2	0.85	40.8	2.0	8.0	338 g.	nil
Kamalas ..	500	24.9	10.1	0.63	40.4	2.0	12.6	593 g.	nil
Narinja ..	240	13.4	9.8	3.0	39.2	2.5	6.5	95 g.	nil
Lime ..	1,000	18.3	9.3	6.5	37.2	2.5	16.0	nil	13.3 Kg.
Grape fruit ..	50	5.6	9.7	4.1	38.8	3.9	2.67	93 g.	nil
Matheepala ..	100	5.8	9.3	6.9	37.2	3.7	3.48	nil	1.52 Kg.

Cost of Manufacture—(Waltair)

Name of fruit.	Cost of fruits.	Cost of sugar.	Cost of acid.	Cost of containers 24 oz.	Cost of labour including skilled (except supervision).	No. of 24 oz. made.	Total cost.	Cost of 24 oz. bottle.
	Rs.	Rs.	Rs.	Rs.	Rs.		Rs.	Rs.
Batavias ..	8-0-0	2-8-0	1-6-0	4-8-0	0-12-0	27	17-2-0	0-10-3
Kamalas ..	10-0-0	3-15-0	2-7-0	7-10-0	1-0-0	46	25-0-0	0-8-8
Narinja ..	12-0-0	2-0-6	0-6-6	4-0-9	0-12-0	24	19-3-0	0-12-9
Lime ..	3-12-0	5-0-0	nil	9-8-0	1-0-0	57	19-4-0	0-5-6
Grape fruit ..	4-0-0	0-13-6	0-6-6	1-8-0	0-8-0	9	7-4-0	0-13-0
Matheepala ..	5-0-0	1-1-6	nil	2-2-6	0-8-0	13	7-12-0	0-9-6

The costs of manufacture of the various juices can be considerably reduced if the preservation of the juices is carried out in places where the fruits are actually grown. Even when higher prices are paid at Waltair for the various fruits, the costs of production as given in the above table still leave a wide margin of profit, taking into consideration the selling price of the citrus juices in the market at Rs.1-8-0 to Rs.2-0-0 per bottle of 24 oz.

It is thus found that the juices from the citrus fruits available locally can be preserved according to the conditions mentioned above with the costs of production recorded. By preserving the juices in the manner described, it is possible to make these valuable juices available in places where these fruits are not grown and in

season when they are not available. Further the process described does not require high initial costs or an elaborate equipment (about Rs.500) and could be successfully employed for harnessing the potential resources of Andhradesa.

BIBLIOGRAPHY

1. A Dictionary of the Economic Products of India by George Watt, Vol. II.
2. Indian Medicinal Plants by Kirtikar and Basu—Vol. I. Second edition.
3. Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Fourth edition, 1935.
4. Indian Journal of Medical Research, 1935.
5. Agriculture and Live-stock in India, 1936.
6. Industrial and Engineering Chemistry, Industrial Edition, 1937.
7. The Indian Journal of Agricultural Science, 1938.
8. Chemistry and Utilization of Indian Fruits (Indian Shaddock)—Thesis submitted to the Andhra University for the M.Sc. degree in 1938.
9. Chemistry and Utilization of common Indian Fruits—Thesis submitted to the Andhra University for the M.Sc. degree in 1939.
10. Proceedings of the Indian Academy of Sciences, 1940.

THE CHEMISTRY OF SOME MEDICINAL OILS

By

S. RANGASWAMI

Though fixed oils have long been known as useful and sometimes essential articles of food they have also been in use since ancient times in the treatment of various ailments. Some of them like olive oil, arachis oil and sesame oil are used in medicine as indifferent oils while others like castor oil and neem oil have specific medicinal effects. The latter category may owe their therapeutic action either to some component which is present in the oil in a chemically combined form as a glyceride or to some active principles which exist in the oil in a state of simple solution.

Of the indifferent oils olive oil holds the most important place in the western system of medicine. It is obtained by expression from the ripe fruits of *Olea Europea*, a small tree cultivated mainly in the Mediterranean countries, California and South Australia. India imports most of her requirements of this oil from Italy and France. Arachis oil (otherwise known as ground-nut or pea-nut oil) is available in India in large quantities at a very cheap price in contradistinction to olive oil which is very expensive. It has the following physical and chemical properties as compared with those of olive oil:—

	Olive oil.	Arachis oil.
Specific gravity at 15°C.	.. 0.916–0.918	0.9165–0.9175
Solidifying point 3°–4°C.	0°–2°C.
Saponification value	.. 185–196	186–196
Iodine value 77–95	83–105
Maumené number, °C.	.. 42–52	45–51
Acetyl number 10.6	9.1
Reichert-Meissl number	.. 0.6	0.5
Unsataponifiable matter	.. 0.4–1.2%	0.5–1.0%

The figures are sufficiently close to justify the assumption that arachis oil can safely replace olive oil for most of the purposes

for which the latter is used. Olive oil is used both internally and externally as a nutrient, as a mild laxative, as a component of enemas and as a vehicle for drugs for injection; it is also a basis for liniments, plasters and ointments. The British Pharmacopoeia in fact allows the substitution of olive by arachis oil in the preparation of liniments, plasters, ointments and soaps in India and certain of the British dominions. It would be a matter for gratification if in India the indigenous arachis oil could completely displace the imported olive oil which frequently is not quite genuine or quite well preserved.

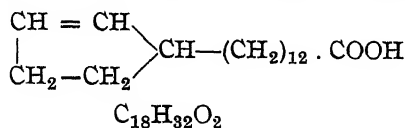
Castor oil is one of the oldest and most important purgatives known. It possesses an advantage over certain other purgative drugs like rhubarb, senna, aloes and jalap in that it does not cause griping as the others do. The purgative action of castor oil is due to the hydroxy acid, ricinoleic acid $C_{17}H_{32}(OH)COOH$ which exists in the oil as a glyceride to the extent of about 90%. When the oil is given by the mouth the ricinoleic acid is set free in the duodenum as a result of hydrolysis and causes purgation. The other fatty acids present in the oil are chiefly palmitic and stearic acids. Apart from the oil which is contained in the kernels a toxic substance of albuminoid nature is also present in the castor seeds. It is called ricin and is not present in the oil to any extent.

For medicinal purposes cold-drawn castor oil is generally preferred since it is comparatively free from odour and taste. The hot-drawn oil on the other hand has a nauseous taste owing to some of the constituents of the husk getting into the oil in this process of extraction.

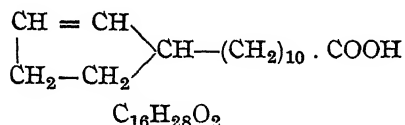
The treatment of leprosy with hydnocarpus and chaulmoogra oils has been practised in India for a long time. Hydnocarpus Wightiana, from the seeds of which hydnocarpus oil is obtained, grows abundantly in Malabar and Taraktogenos Kurzii, the source of chaulmoogra oil, is grown in Eastern Bengal, Assam and Upper Burma. Certain other species of Hydnocarpus have also been found to yield oils useful in leprosy.

In 1905 Power and Barrowcliff¹ examined hydnocarpus oil and found that it consisted almost entirely of the glycerides of two

acids that had not till then been met with in any other oil. These two acids were optically active, unsaturated and had a carbon ring; they were designated hydnocarpic and chaulmoogric acids. Their constitutions are as shown below, chaulmoogric acid being a higher homologue of hydnocarpic acid:



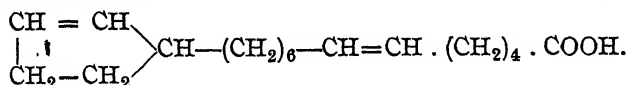
Chaulmoogric acid.



Hydnocarpic acid.

The discovery that these two acids are responsible for the curative action of the natural oil in leprosy has led to certain developments in the utilization of the oil for therapeutic purposes. The ethyl-esters and sodium salts of the acids have been found more convenient to use and have displaced the natural oil to a large extent.

The chemistry of the anti-leprosy oils has been very intensively studied during the past few years. Working at the International Leprosy Clinic at Rio De Janeiro, Cole and Cardoso have reinvestigated several of them and have discovered a number of new acids which had somehow been missed by the previous investigators. The existence of a small proportion of an acid with high iodine number in 'a Chaulmoogra oil' had long been known² and in 1928 Andre and Jouatte³ reported the presence of an acid ('gorlic acid') in 'gorli oil' (*Oncoba Echinata*), which however could not be obtained pure. A similar acid was discovered by Paget⁴ in *Carpotroche Brasiliensis*. Though Paget could not get it pure he succeeded in establishing its constitution as 'dehydro-chaulmoogric acid'



In 1938 Cole and Cardoso⁵ obtained the acids of Andre and Jouatte and of Paget in a pure state and found that they were identical; the name 'gorlic acid' first suggested by Andre and Jouatte has been retained for it. This new acid has since been shown to be present even in the oil from *Hydnocarpus Wightiana*⁶. This oil has also been subjected to a very thorough examination⁶ as a result

of which the authors have been able to isolate two new acids (lower homologues of hydnocarpic acid) and establish the presence of two other homologues which were obtained 70·5% and 42% pure respectively. All the four new acids were unsaturated and optically active; the constitutions suggested for them together with the names proposed are given in the following table:

(Chaulmoogric acid	$C_{18}H_{32}O_2$)
(Hydnocarpic acid	$C_{16}H_{28}O_2$)
Alepric acid	$C_{14}H_{24}O_2$
Alepyric acid	$C_{12}H_{20}O_2$
Aleprestic acid (70·5% pure)	$C_{10}H_{16}O_2$
Aleprolic acid (42% pure)	$C_8H_8O_2$

The complete analysis of the mixed fatty acids from the oil of *Hydnocarpus Wightiana* has also been reported by the above authors for the first time and is reproduced below:

Hydnocarpic acid	48·7%
Chaulmoogric acid	27·0%
Gorlic acid	12·2%
Oleic acid	6·5%
Palmitic acid	1·8%
Lower homologues of chaulmoogric acid (alepric, alepyric, aleprestic and alep- rolic and unidentified acids)	3·4%
Loss	0·4%
			<hr/> 100·0

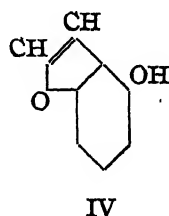
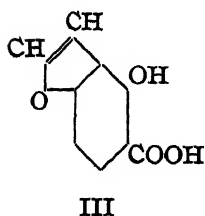
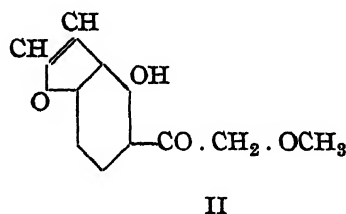
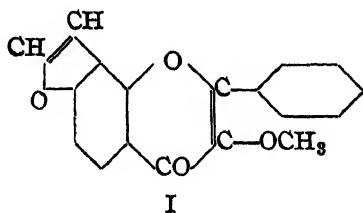
The importance of cod-liver oil in nutrition was recognized long ago. It is the most easily assimilable of all oils and is of particular benefit in the malnutrition of children and in wasting diseases such as tuberculosis. It contains a large proportion of unsaturated fatty glycerides, mainly those of clupanodonic acid, and small quantities of glycerides of palmitic and stearic acids. It was formerly believed that the unsaturated character of the fat was the most important factor in the use of cod-liver oil in nutrition; but now it is well recognized that the most important medicinal constituents

of the oil are vitamin A (growth-promoting and anti-infective) and vitamin D (antirachitic). The vitamin activity of cod-liver oil varies widely in different samples but an average sample contains about 2000 units of vitamin A and about 100 units of vitamin D per gramme. The vitamins are present exclusively in the unsaponifiable fraction of the oil which forms about 1% and is composed of cholesterol (0.5% based on the weight of the oil), batyl alcohol, a hydrocarbon and vitamins A and D. The recognition of the vitamins as the most important constituents of the oil has led to the introduction into therapeutics of cod-liver oil concentrates which are very useful in the treatment of certain conditions requiring the administration of large quantities of cod-liver oil. These concentrates may be prepared from cod-liver oil by saponification with alcoholic potash, extraction of the unsaponifiable matter with ether and removal of the cholesterol from the ether-soluble fraction. Their potency with regard to the two vitamins is approximately 200 times that of the original oil. It is again because of its high vitamins A and D content that halibut-liver oil has to a large extent taken the place originally held by cod-liver oil.

Pongamia Glabra known as 'karanja' in Sanskrit is a small tree with glabrous bright green foliage common to many parts of India particularly near the coast. The leaves, bark, seeds and especially the oil obtained from the seeds have all been used in Hindu medicine from very early times for skin diseases, rheumatism and whooping cough.

While investigating the non-glyceride portion of pongamia oil Limaye⁷ isolated a crystalline bitter compound to which he assigned the name 'karanjin'. It is present in the oil in a state of solution. By shaking the oil with alcohol Limaye obtained a 0.33% yield of karanjin, but it has recently been found⁸ that the yield can be considerably improved (0.9%) by adopting the method of continuous extraction with hot alcohol. Clinical experiments showed that it is karanjin which is responsible for the curative property of pongamia oil in leucoderma⁸; consequently preparations of karanjin suitable for therapeutic application have recently been evolved in these laboratories⁹.

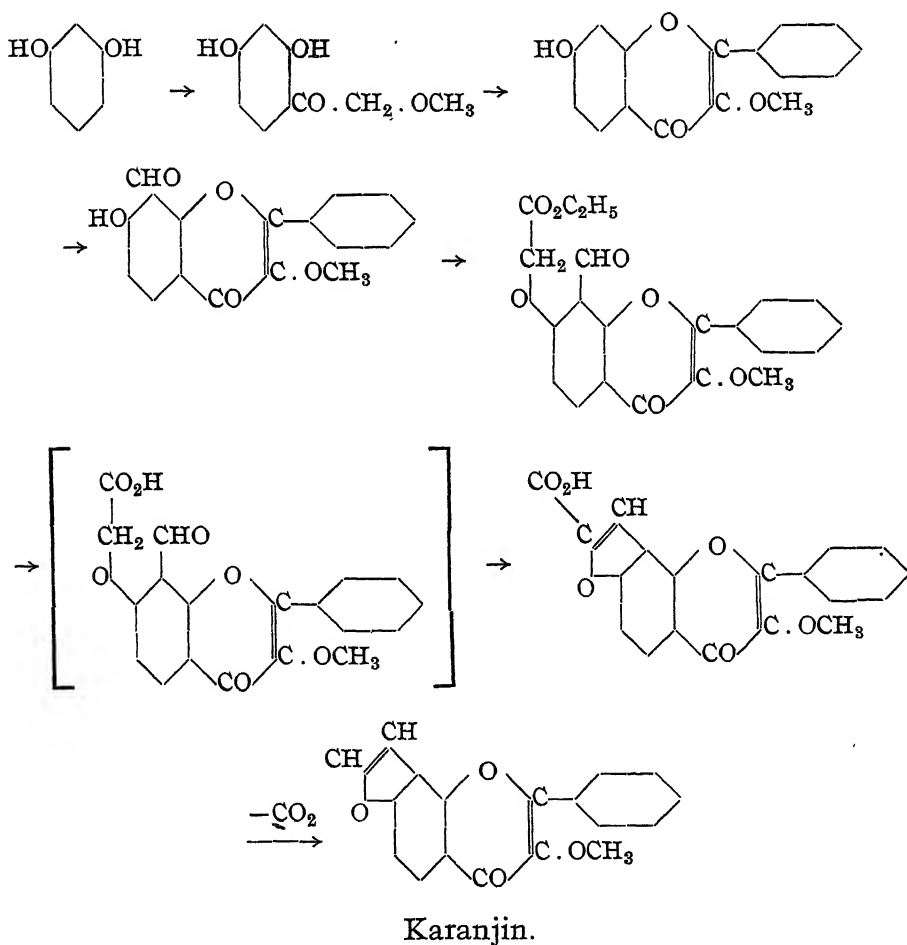
The constitution of karanjin has engaged the attention of three laboratories in India and though according to the available evidence there can be no ambiguity regarding the structure of the molecule rigid proof is still lacking. Working at Poona Limaye showed that karanjin has the molecular formula $C_{18}H_{12}O_4$, that it has a methoxyl group and that it belongs to the flavone group of compounds. Also by degradation experiments using potash he isolated four products: (1) a hydroxyketone having the formula $C_{11}H_{10}O_4$ (II), (2) karanjic acid, $C_9H_6O_4$ (III), (3) karanjol, $C_8H_6O_2$ (IV), and (4) benzoic acid. Karanjol could be obtained by the decomposition of karanjic acid and could be easily converted into the acid by boiling with aqueous sodium bicarbonate. It was considered to be 4-hydroxycoumarone and this idea was confirmed by synthesis. The constitution of karanjin was therefore represented as that of 3-methoxyflavono-7:8-furan (I) ¹⁰.



More recently Manjunath *et al.*¹¹ working at Bangalore succeeded in converting the ketone (II) into karanjin (I) by the Allan-Robinson method using benzoic anhydride and sodium benzoate, thereby definitely proving that karanjin is a flavone derivative. But though the constitutions of (III) and of (IV) have been definitely settled both analytically and synthetically the relation between (II) and the simpler members (III) and (IV) has not been established as

yet, so that the constitution of karanjin cannot be taken as proved beyond doubt.

The total synthesis of karanjin with a view to definitely establish its constitution has been attempted in the Chemistry Department of the Andhra University on the lines indicated below¹²; but the last stage in the synthesis, viz., the elimination of carbon dioxide has not yet been achieved.



Very recently the occurrence in pongamia oil of a phenolic compound also belonging to the flavone group was discovered¹³.

The chemical constitution of this new entity which has the molecular formula $C_{18}H_{14}O_4$ is under investigation.

The neem tree, *Melia Azadirachta*, grows throughout the greater part of India and Burma. Almost every part of this tree has been used for medicinal purposes in India. The oil obtained from the seeds is used as an antiseptic, anthelmintic and insecticide and also in the treatment of skin diseases.

Our knowledge of the chemistry of neem oil is far from satisfactory. Much work has been done during the last twenty years but there has been no unanimity of opinion regarding the active principles contained therein. Some of the earliest reports regarding the nature of the chemical compounds which impart to neem oil its curative properties may be dismissed as mere speculations. The subsequent investigations generally ascribed the virtues of neem oil to one or more of the following groups of compounds. They are described below with relevant comments.

(a) *Acids existing as glycerides*.—It was Chatterjee and Sen ¹⁴ who first claimed to have isolated an acid called margosic acid which had the formula $C_{22}H_{40}O_2$ and which was supposed to exist in the oil as a glyceride to the extent of 24%. Subsequent investigators could not confirm this observation and finally Roy and Dutt ¹⁵ showed that margosic acid was not a single substance but a mixture of oleic and linolic acids.

Further evidence in favour of the opinion that the active principles of neem oil are not of the nature of glycerides may also be adduced from the observations of Child and Ramanathan ¹⁶, Narasimhamurti (M.Sc. thesis presented to the Andhra University) and Hilditch and Murti ¹⁷ according to whom the mixed fatty acids of neem oil are composed only of the common fatty acids like palmitic, stearic and oleic present in all edible oils.

Recently however Khuda *et al.* ¹⁸ have claimed to have isolated four new acids from the glyceride portion of neem oil. Two of them having the formulae $C_{14}H_{28}O_2$ and $C_{16}H_{32}O_2$ are saturated. The other two which are unsaturated have the formulae $C_{15}H_{28}O_2$ and $C_{19}H_{32}O_4$; of these the first belongs to the oleic acid series

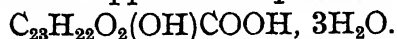
and the second to the cyclic series of which hydnocarpic and chaulmoogric acids are the well-known representatives. The possible rôle which these newly discovered acids play in neem oil therapy is a matter for future investigation.

(b) *Volatile sulphur compounds*.—Watson and co-workers¹⁹ found that on prolonged steam-distillation of neem oil a volatile sulphur compound with a very disagreeable smell slowly distilled over. The volatile oil thus prepared was found to have the molecular formula $C_{21}H_{44}S$; it was not a mercaptan as it did not give a precipitate with lead acetate. Recently Khuda *et al.*¹⁸ have obtained from the steam-distillate a colourless mobile liquid (neemola) which has the molecular formula $C_{15}H_{30}O_3S$. The point to be noted here is that this compound contains oxygen in the molecule whereas Watson's preparation did not.

(c) *Compounds extractable with water*.—By boiling crushed neem seeds with water, Watson and co-workers¹⁹ obtained a non-bitter organic sulphur compound having the formula $C_{13}H_{24}O_7S_2$. Later Sen and Bannerjee²⁰ extracted the oil itself with water and obtained a compound having the formula $C_{55}H_{81}O_3S$ together with a non-bitter fraction free from sulphur. More recently Khuda *et al.*¹⁸ have isolated from the steam-distilled oil a sulphur-free compound 'which analysed for a glucoside of the formula $C_{28}H_{48}O_{10}$ '. If this be correct it would be the first instance of a glucoside existing in solution in a fixed oil.

(d) *Other compounds*.—Warden²¹ extracted neem oil with alcohol and reported the presence in the extract of a neutral resin, an acid resin and a principle of alkaloidal nature. Watson and co-workers¹⁹, on the other hand, saponified the oil and after removal of the soap obtained a crude resin by acidifying the lye. Fractionation of the resin through the use of different solvents like absolute alcohol, benzene, petroleum ether and chloroform gave two amorphous compounds melting at 85–88° and a crystalline compound swelling at 128° and melting at 221–222°. They all possessed the same empirical formula C_3H_4O ; but the amorphous compounds had a molecular weight of 275 which corresponds to the formula

$C_{15}H_{20}O_5$, while the crystalline compound which was called margo-sopicrin by these authors appeared to possess the formula



From the foregoing account it is clear that our knowledge of the chemistry of neem oil is quite nebulous and requires complete clarification with a view to correlate the findings of different investigators. Some attempt in this direction was projected in the Chemistry Department of the Andhra University and though our results did not quite fulfil the object with which the experiments were set afoot they brought out certain salient points which are briefly set forth below:

Alcoholic extraction of the oil yielded an amorphous powder which could be roughly separated into two components. These could also be obtained, though in smaller yield, by extracting the oil-cake with alcohol. They contained practically no sulphur and were markedly bitter to the taste. They were non-toxic to fresh water fish and to earthworms in concentrations of 1 in 5,000 and 1 in 1,000 respectively and hence are not likely to be the cause of the insecticidal and anthelmintic qualities of neem oil. When the oil was allowed to stand undisturbed for some months a deposit composed of these bitter principles, resins and free fatty acids was obtained at the bottom of the containing vessel; the supernatant oil thereafter did not contain any extractable matter other than traces of fatty acids.

REFERENCES

- ¹ Power and Barrowcliff, J.C.S., 1905, 884-896.
- ² Dean and Wrenshall, J.Am.C.S., 1920, 2626.
- ³ Andre and Jouatte, Bull. Soc. Chem., 1928, 347.
- ⁴ Paget, J.C.S., 1937, 955.
- ⁵ Cole and Cardoso, J.Am.C.S., 1938, 612-614.
- ⁶ " " " " *ibid.*, 1939, 2349-2353.
- ⁷ Limaye, Abst. Ind. Sci. Cong., 1925, 118.
- ⁸ Rao, Rao and Seshadri, Proc. Ind. Acad. Sci., 1939, A, X, 65.
- ⁹ Rangaswami and Seshadri, Ind. J. Pharmacy, 1940, II, 1.
- ¹⁰ Limaye, Rasayanam, 1936, 1-14; 1937, 119.
- ¹¹ Manjunath, Seetharamiah and Siddappa, Ber., 1939, 93.
- ¹² Rangaswami and Seshadri, Proc. Ind. Acad. Sci., 1939A, IX, 259.
- ¹³ Rangaswami and Seshadri, Curr. Sci., 1940, 179.

- ¹⁴ Chatterjee and Sen, Ind. J. Med. Res., 1920, VIII, 356.
- ¹⁵ Roy and Dutt, J. S. Chem. Ind., 1929, 48, 333T.
- ¹⁶ Child and Ramanathan, *ibid.*, 1936, 55, 124T.
- ¹⁷ Hilditch and Murti, *ibid.*, 1939, 58, 310T.
- ¹⁸ Khuda, Ghosh and Mukherjee, J. Indian C.S., 1940, 189.
- ¹⁹ Watson, Chatterjee and Mukherji, J.S. Chem. Ind., 1923, 42, 387T.
- ²⁰ Sen and Bannerjee, J. Indian C.S., 1931, 773.
- ²¹ Warden, Pharm. J., 1888, III, 325.

Note added in proof.

Since writing the article karanjic acid (formula III on page 186) has been converted into the ketone II (on the same page) by unequivocal methods (*vide* Seshadri and Venkateswarlu, Proc. Ind. Acad. Sci., 1941 A, 13, 404). Thus the complete synthesis of karanjin (I) has been effected and the constitution of karanjin is now well established.

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STUDY III OF DR. C. R. REDDY BY
MR. K. RAM MOHAN SASTRI.

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C. D. Reddy
24-8-1940

Ram Mohan Sastri
WALTAIR

LICHENS AND THE CHEMISTRY OF THEIR CONSTITUENTS

By

V. SUBBA RAO

The lichens, known in Sanskrit as Sailaja or Saileya, Charila in Hindi, Kulpasi in Tamil and Rathipachi or Rathipuvvu in Telugu, form a very interesting and large order of lowly plants, resistant to extremes of heat and cold and probably with a wider distribution than any other form of plant life. They are common objects on walls and rocks and on trees, to which some of them do much injury. Though the majority are not parasites, they shelter numerous forms of insect life and when present in abundance on barks of trees prevent them from performing their functions. The lichens are exceedingly diversified in their form, appearance and texture, and more than three thousand species of them have been recorded by the botanists. For many centuries they were regarded as separate entities like ferns, fungi and algae until 1866, when De Bary showed them to have a dual nature, each lichen being composed of a fungus and one or more single celled or thread-like algae. Both these partners lead a symbiotic life, the green algal component performing the photosynthetic function and the fungal partner mainly the reproductive function. According to the nature of their external form (called Thallus) they are divided into three categories: (1) Crustaceous lichens, with crust-like bodies, (2) Fruticose lichens, with tuft-like bodies, (3) Foliaceous lichens, with pendulous and ribbon-like bodies. Though self-supporting, lichens exhibit a considerable choice of habitat, and form more or less constant associations of lichens or with other plants. By their delicate filaments they cling to the rock surfaces which they gradually penetrate and disintegrate. The chief ecological factors are the types of substratum and the associations of the plants consequently depend upon them. As in other plant communities, there is a struggle for place and light. Crustaceous species are invaded and ousted by those of thicker or squamulose

thallus or by the larger foliose species. Some mischance may dislodge them all and colonization begins afresh. Lichens are rare or absent in the neighbourhood of large towns or industrial areas owing to the smoke-laden and contaminated atmosphere.

Many species of lichens are of economic value. They have found use in various ways as dyestuffs, foodstuffs and material for making drugs. Excepting the work of Chopra on the lichens of the Sikkim Himalayas, not much work seems to have been done on Indian lichens of economic value. Due to the high content of carbohydrate some lichens in the arctic regions form an important source of animal food and have more than once saved the lives of explorers whose provisions were exhausted. The most important of these is the Reindeer Moss (*Roccella tinctoria*) which grows on rocks by the coast and is an important source of litmus. Certain other species are well known for their property of yielding colouring matters like orchil and cudbear. Even in medicine the lichens have found good use in the past. Some very bitter species such as '*Pertusaria fraginea*' served as a substitute for quinine. '*Cetraria islandica*' or 'Iceland moss', owing partly to its gelatinous consistency, has been used with good effect in chest troubles, and is now the only lichen recognized in the British Pharmacopoeia. It has been recorded by Watt that the true orchil (*Roccella tinctoria*) was to be found in Ceylon where it grows on the stems of certain palms and that samples of this had also been sent to the colonial and Indian exhibition in 1886, as a drug from Madras. Many species enjoyed a great reputation as demulcents, febrifuges, astringents, tonics, purgatives and anthelmintics. Special mention may be made of *Peltigra canina* which has been regarded for a long time as a specific for hydrophobia, and *Platysma juniperinum* which was considered to be very effective in cases of jaundice. Several species of the genus '*Cetraria*' occur in India and investigation may reveal certain of these to be endowed with similar curative properties as the lichen '*Cetraria islandica*'. The lichens that are described to have been in use as medicines in India are of the *Parmelia* genus—*Parmelia kumtschadalis*, *P. perlata* and *P. perforata*. The first is stated to be a remedy for headache in the form of smoke and also a good

cephalic snuff in the form of powder. It is widely administered by Hakims in disorders of the stomach, dyspepsia, vomiting, pain in the liver, etc. The two other lichens were reputed to be good diuretics during the first half of the nineteenth century, the administration being effected by first boiling the lichen with water, beating it into a pulp and applying it as a poultice over the renal and lumbar regions. In the early part of this century many other species have been used as substitutes for salve bases, glycerol, soap and fat, for the reduction of bitter taste in drugs, especially laxatives, and also as culture media for bacteria. A recent application of lichens in medicine is through the phenols, phenol carboxylic acids and esters derived from lichen substances which are used as antiseptics with encouraging results. Among the various compounds studied, Orsellinic esters and compounds of the divarinol type were found to possess a strong antiseptic action on 'Shoyu' (Soyabean sauce). Finally, it may be interesting to mention that besides the above uses, various species of lichens have been employed in perfumery for cold creams and as bases in hair dressing. *Cetraria islandica* (Iceland moss) and *Cladonia rangiferina* were employed for the production of alcohol also. They also find application as good substitutes for gum arabic and cork. The dye-yielding properties of some lichens, e.g., *Roccella tinctoria*, *Lecanora tartarea*, etc., give them the importance that they have. The colouring matters orchil and cudbear and the indicator litmus, which is commonly used in the laboratory, are prepared from these lichens. The litmus obtained from these finds use in commerce as a colouring agent for vinegar, to which it imparts a red colour due to the acid present. Recently it has been found by us that a species of lichen belonging to the genus *Roccella* occurs abundantly in Waltair on cashew-nut, mango, *Pongamia-glabra*, tamarind and banyan trees. A sample of this species sent to Kew (London) was identified as '*Roccella montagnei*'. It has been examined by us in these laboratories for its tinctorial qualities and was found to yield the colouring matters orchil and litmus in good yield. Another lichen, known as 'Rathipuvvu' (meaning rock-flower in English) and occurring abundantly in certain rocky areas in the Bellary and Cuddapah districts, has also been completely

examined in these laboratories and has been found to contain the essential compounds necessary for the production of litmus in good yield. This lichen sample, on being sent to the Kew gardens for identification, was pronounced as almost identical with *Parmelia abessinica* (Kremp). Of the lichens available in India, this lichen seems to be the only one to be used as a food material to an appreciable extent. A certain amount of trade is also carried on with this lichen. Merchants pay a certain seigniorage for export and sell the lichen at a fairly good price (about Rs.10 per maund), thus making a decent profit as the cost of collection of the lichen is very low.

The chemical constituents of lichens form a distinct class of chemical compounds and our earlier chemical knowledge about these is mainly due to the work of Knop, Rochleder, Heldt, Schunck, Schmidt, Stenhouse, etc., whereas for the later very numerous investigations we are chiefly indebted to the chemists Oswald Hesse, Wilhelm Zopf, St. Pfau, Emil Fischer, Yasuhiko Asahina and others. The lichen acids show a wide range of chemical formulae and a great variety of crystalline form. Many of them are bright yellow, orange or red, and give the clear pure tone of colour to many lichens. Some of these compounds are rare while others are widely distributed. A very large number of new compounds have been isolated and described, the constitutions of which in most cases are as yet undecided. On the other hand, considerable advance has been made as regards the exact structure of some of the more common constituents, viz., Atranorin, Erythrin, Lecanoric acid, Evernic acid, Ramalic acid and Barbatic acid. Examination reveals that both organic and inorganic substances are present in lichens. The organic substances occurring in lichens are (1) lichenin and iso-lichenin which are a special type of carbohydrates specific to lichens, (2) starch which occurs exterior to the walls of the algae in greatest amount in autumn and least in spring, (3) certain acids of the depside and depsidone types which have seldom been found elsewhere in nature except in the tannins, (4) the plastid pigments, chlorophyll, carotene, etc. which exist in small quantities only, (5) certain sugar-alcohols, and (6) waxy and resinous matter. The inorganic consti-

tments form 8–10% of the lichen. The ash contains usually the alkalis, lime and magnesia, alumina, silica, manganese, iron, chloride, phosphate, sulphate and carbonate.

The following classification of lichen products according to their chemical structures is due to Prof. Y. Asahina.

The lichen compounds are divided into three main series—(1) the fatty series, (2) the aromatic series, and (3) products of unknown constitution. The first two series are again subdivided as indicated below.

(1) *Fatty series* :—

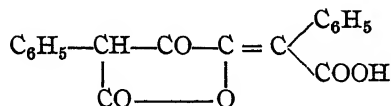
(a) *Fatty acids and lactones*.—These are colourless substances, soluble in alkali carbonates and saponifiable by alkali. They give no colour with ferric chloride or bleaching powder. Some of the compounds which belong to this series are protolichestic acid, lichestic acid, caperatic acid, etc.

(b) *Neutral compounds not hydrolyzed by alkali*.—These are colourless crystals, which are insoluble in alkali in cold and hot, and give no colour with ferric chloride or bleaching powder. Zeorin is the main representative of this series.

(c) *Alcoholic sugar*.—Among these the more common compounds occurring are erythritol, mannitol, *d*-arabitol, etc.

(2) *Aromatic series* :—

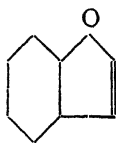
(a) *Pulvinic acid derivatives*.—These are yellow crystalline substances, slightly soluble in ether and alcohol and easily in chloroform and carbon di-sulphide and bearing a resemblance to pulvinic acid in structure.



Pulvinic acid.

Some of the compounds are stictaurin, calycin, rhizocarpic and rhizocarpinic acids.

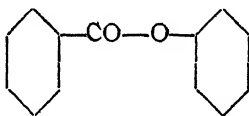
(b) *Coumarone derivatives*.—The compounds belonging to this group contain the coumarone structure



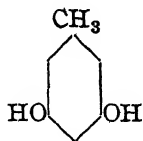
usnic acid being the typical representative. It was formerly supposed to be an acetoacetic ester derivative, but later Schopf and co-workers characterized it to be a quinol like phloroglucinol derivative. The compound was more closely studied in recent times by Robertson and co-workers who found that it consists of a phloroglucinol ring attached to a coumarone ring.

(c) *Thiophanic acid group*.—The nature of the compounds of this group is not yet completely cleared up. They are yellow substances and in an alcoholic solution give with ferric chloride a light green to dirty-blue colouration. Thiophanic acid, thiophaninic acid, pulverin and subauriferin are some of the compounds belonging to this group.

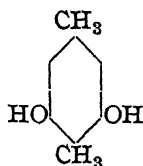
(d) *Depside group*.—Compounds of this group have the depside structure



and are the derivatives of *p*-benzoyloxybenzoic acid. They are again classified under two sub-groups, according as they are derived from orcinol or β -orcinol.

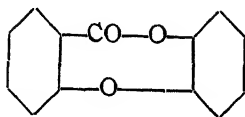


Orcinol.

 β -orcinol.

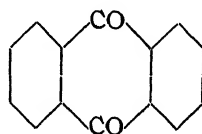
Lecanoric acid, evernic acid, barbatic acid and diffractaic acid are some of the members of this group.

(e) *Depsidones*.—Compounds of this group contain the depsidone skeleton



and are again subdivided into orcin derivatives and β -orcin derivatives. Physodic acid, alectoronic acid, protocetraric acid, cetraric acid, etc., belong to this group.

(f) *Anthraquinone derivatives*.—Compounds of this group contain the anthraquinone skeleton



and are yellow or red to brown crystalline compounds which turn purple to blue-violet with alkali. The main representatives are parietin, solorinic acid, rhodocladonic acid and nephromin.

Of the two lichens examined in these laboratories, the lichen *Roccella montagnei*, which occurs abundantly in Waltair, was examined by Hesse and Ronceray about the year 1900, but the methods that they employed could not yield complete information regarding the composition of the lichen. They reported the isolation of three components, erythrin ($C_{20}H_{22}O_{10}$, H_2O), oxyroccellic acid ($C_{17}H_{30}O_5$) and orcinol ($C_7H_8O_2$, H_2O). A thorough examination of the Indian sample made in these laboratories using a series of solvents in succession for purposes of extraction and also starting with samples obtained during different parts of the year and from various locations revealed the presence of erythrin, orcinol, roccellic acid ($C_{17}H_{32}O_4$) and also erythritol ($C_4H_{10}O_4$), lecanoric acid ($C_{16}H_{14}O_7$, H_2O) and isolichenin. Oxyroccellic acid, however, could not be found during the course of our work. The lichen has been found to differ markedly in composition, depending upon the season. During the wet season it is found to contain erythrin, orcinol and erythritol; and during the dry season no erythrin is found and besides orcinol and erythritol, roccellic and lecanoric acids make their appearance.

No work seems to have been done on the second lichen examined in these laboratories. However, several species of the genus *Parmelia* have been examined in detail by previous workers. A preliminary study of the lichen showed that it contained carbohydrates to the extent of about 30%, nitrogen 0.98%, moisture 13.49% and ash 9.75% consisting of phosphates, silicates and carbonates of iron, calcium and magnesium. Subsequent extraction of the lichen with several solvents used in succession yielded the compounds atranorin, lecanoric acid, β -methyl ether of salazinic acid and lichenin. Various synthetic experiments have been carried out with the fission products of these compounds and a number of hydroxycoumarins obtained.

The compounds erythrin and lecanoric acid present in these lichens growing in South India make them highly useful sources for the commercial manufacture of litmus. On hydrolysis and decarboxylation both erythrin and lecanoric acid yield orcinol which when subjected to the combined influence of air, ammonia and potassium or sodium carbonate is converted into azolitmin (the colouring matter of litmus), the alkali salts of which are blue. It has been found by us that litmus can be prepared in good yield from both these lichens. The abundance and cheap cost of both the lichens thus make them very promising sources for this dyestuff which can be easily made to replace the imported material.

REFERENCES

1. Chopra. *Lichens of Sikkim Himalayas* (Punjab University Press).
2. Watt. *A Dictionary of Economic Products of India*, Vol. IV, 636.
3. Perkin and Everest. *The Natural Organic Colouring Matters*, 529-566.
4. Piorowski. *Ber. Pharm. Ges.*, 1916, 26, 192-198.
5. Huzikawa. *J. Pharm. Soc. Japan*, 1939, 59, 240-247.
6. Asahina. *Acta Phytochemica*, 1934, 8, 34-35.
7. Hesse. *J. Pr. Chem.*, 1898, (ii), 57, 232.
8. Ronceray. *Bull. Soc. Chim.*, 1094, (iii), 1097.

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CRYSTALLINE BITTER PRINCIPLES OF CITRUS FRUITS. ISOLATION OF A NEW MEMBER OF THE GROUP, AURANTIN

By

K. C. PATNAYAK and T. R. SESHADRI

Amongst the enormous variety of fruits available in the world those belonging to the citrus group occupy the foremost place. They are valued highly not only for their delicious taste but also for their capacity to cure various ailments to which the human race is subject. It has therefore been an interesting enquiry to examine the chemical components which are responsible for their virtues. Apart from the high percentage of water which is aptly expressed by the term juiciness, the main skeleton of the fruits consists of cellulose and related chemical compounds known as hemicelluloses and pectins. The delicate aroma arises out of the existence of sweet-smelling essential oils. In regard to the taste of these fruits the two most important chemical components which play a decisive rôle are the sugars and the organic acids. These can be easily obtained, crystalline, sucrose and glucose being the most common of the sugars and citric acid the most important of the organic acids present in citrus fruits. One of the comparatively recent discoveries in regard to the acid components is that of ascorbic acid, otherwise known as vitamin C. The citrus fruits form the most important and palatable source for this vitamin and our preference for particular varieties of the citrus largely depends on their ascorbic acid content.

Bitterness as a taste is not unwelcome under all conditions. Barring certain classes of people who have developed a taste for bitter things it may be said that a judicious admixture of bitterness improves other tastes such as the sweet and the sour. Amongst the citrus there seems to exist no fruit which is entirely devoid of bitterness. Much of the commercial value of these fruits depends

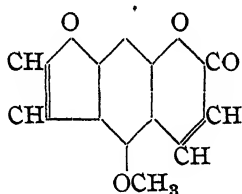
upon the extent to which the bitter principles occur. It is now realized that bitter principles are present practically all over the fruit in more or less quantities; they are, however, found markedly in the peels, the rags which consist of the placenta and the vascular bundles and the seeds. The juice is ordinarily free from them to a great extent and acquires the bitter components during the pressing of the juice from the crushed cells of the peels and the rags. A knowledge of these bitter principles is not only interesting to the chemist who is eager to unravel the mysteries of nature but is also of importance in industries where these fruits are employed. The valuable discovery that the bitter substances can arise from non-bitter compounds or can be converted into such compounds under suitable conditions can be mentioned in this connection.

The crystalline compounds which produce a bitter taste and which have so far been obtained from various types of citrus fruits belong to different groups of organic compounds. There is a large possibility of utilizing the occurrence of these compounds in the botanical identification of species in the citrus fruits. Botanists have often been meeting with great difficulty in correctly identifying the large number of varieties that have been brought into existence due to cultural and other changes. As in many other groups of plants here also a study of the chemical composition and the occurrence of characteristic chemical compounds may be highly useful in simplifying the work of identification. But this aspect of study which naturally requires a laborious collection of analytical data has not been undertaken so far. In this connection it may be mentioned that there is a possible chance of making mistakes and missing the bitter taste of the compounds when they are in a crystalline condition. In a large number of cases the pure crystalline samples are insoluble in water and consequently in the saliva and hence do not produce the sensation of bitterness. But when they are brought into solution at least to a small extent using very dilute alcohol and then tested their bitter taste becomes evident.

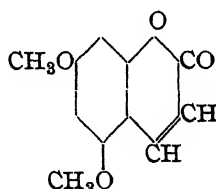
As a rule the bitter compounds contain considerable amount of oxygen besides carbon and hydrogen in their molecules. They all come under the category of carbonyl compounds. They have been

classified here in four different groups and the most important members belonging to each group are mentioned.

1. *The coumarin group*.—Bergapten and limettin have been known to chemists for nearly a hundred years. Still it was only recently that the constitution of bergapten was definitely established by the synthesis of the substance by Howell and Robertson¹ and by Spath and his co-workers². Bergapten is also known as 'bergamot camphor'; it is obtained from the peels of acid lime known as citrus bergamia or bergamoti. It melts at 188° and has the constitution of 5-methoxycoumarino-7:6-furan (I). The oil of bergamot is a component of many of the preparations used as insecticidal sprays. This is due to the fact that bergapten is an insect-poison. Limettin occurs in citrus limetta; it can be obtained as colourless prisms melting at 147°. It is the important component of the oil of lemons. Its presence is easily recognized by the fact that it fluoresces in sulphuric acid solution, the colour of the fluorescence being blue-violet. Its constitution is known to be that of 5:7-dimethoxycoumarin (II). The more recent discoveries in this group are bergaptol and bergamottin from bergamot oil and aurapten from bitter orange peels³.



I. Bergapten.

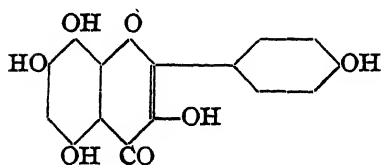


II. Limettin.

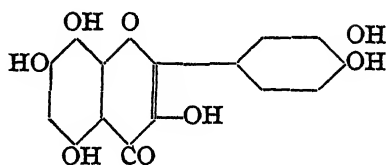
The above compounds belong to a large group of naturally occurring coumarins which have been recently found to be present in various plant materials many of which are official drugs. They are usually referred to as fish-poisons and are found to be good insecticides. To some extent they have been employed as anthelmintics and for the treatment of various skin conditions. The crystalline compounds psoralen and isopsoralen⁴ which have been found in the Indian drug, psoralea corylifolia, in the angelica root and in the fig tree leaves come under this category.

2. *The flavanone group*.—The earliest substance to be known under this category is probably naringin (III). It is intensely bitter, possibly one of the most bitter of chemical compounds known to us. It has the advantage of being easily soluble in water and hence even a very small quantity of it is able to exhibit its bitterness very markedly. It has been found to be a component of the grape fruit very commonly available in America and since it occurs to a very high concentration in the peels and rags of this fruit which is worked up on a large scale in industry, naringin is now obtained commercially from this source. The final details of its constitution have been worked out two years ago in our laboratories ⁵. Amongst the number of citrus fruits that have been analyzed here recently naringin has been found to be present in the peels of the Indian shaddock and in 'Matheepala' (citrus decumana). At this stage an interesting point may be mentioned. In the botanical genus, citrus, there is great difficulty in identifying species and varieties due to the large variations that have been brought about by cultivation. There has been difference of opinion regarding the species to which 'Matheepala' belongs. According to Gamble and some others it belongs to citrus decumana though some others would place it under citrus medica. This finding of Gamble is supported by the isolation of naringin from the peels of the fruits since this bitter principle is characteristic of the decumana species of the citrus.

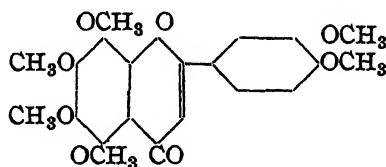
The closely related compounds hesperidin (IV) and eriodictyn (V) have assumed enormous importance during the past few years as the result of the discovery by Brückner and Szent-Gyorgyi ⁶ that these form the components of what they call vitamin P, which is responsible for curing pathological fragility and permeability of capillary walls to plasma proteins. They are found to occur very widely in most citrus fruits though in small concentrations. In spite of their close resemblance in chemical structure to naringin they exhibit only a mild bitter taste. The relationship between the three related compounds is expressed in the following formulae. A fourth member of this group called citronin (VI) has been isolated by



IX. Herbacetin.



X. Gossipetin.



XI. Nobiletin.

Nobiletin is present in the peels of citrus nobilis obtained from Chunking in Western China. Tseng¹¹ who reported its isolation in 1938 obtained it as light yellow crystals melting at 134°. Its constitution as the methyl ether of a hexahydroxy flavone has been suggested by Tseng and Robinson¹². A very interesting point that emerges out of these discoveries is that in the citrus peels the plants possess a very efficient mechanism for methylation and hence these compounds are completely methylated. That limettin and bergapten are also methyl ethers may be recalled at this stage though they have not got in their molecule so many hydroxyl groups methylated as are found in tangeretin and nobiletin. Mention can also be made of highly methylated flavones occurring in well-known drugs. A number of these have been found recently, e.g., calicopterin, a yellow anthelmintic compound isolated from calicopteris floribunda by Ratnagiriswaran, Sehra and Venkataraman¹³ and later found to occur in digitalis thapsi¹⁴. This has four methoxyl groups and two hydroxyl groups in the molecule. Gardenin obtained from gardinea lucida (Dikamali gum), tambulin from zanthoxylum acanthopodium and eryanthin from blumea eriantha by Bose *et al.*¹⁵ are similar in having a large number of methyl ether groups, but there is not the complete methylation as has been realized in the citrus compounds.

4. *Compounds of unknown constitution.*—Under this category come a well-known pair, limonin and isolimonin, both having the

same chemical composition, $C_{26}H_{30}O_8$. They exhibit very similar properties and obviously have very similar chemical constitution. But for their sparing solubility they can be said to be highly bitter and they can contribute to a large extent to the bitter taste of fruits. Limonin was originally obtained from lemon seeds and has been known for a considerable number of years. But it was first studied in some detail by Koller and Czarney¹⁶ in 1936 who also obtained isolimonin from lemon seeds. Feist and Overberg¹⁷ isolated limonin from orange kernels also. As a result of work done in our laboratories it has been realized that limonin is invariably present in citrus kernels accompanied by isolimonin in most cases¹⁸. Strangely these have also been found to occur in the juices of Valencia and Navel oranges¹⁹. Their chemical constitutions are very complex and are quite unsettled. But it is known that they contain lactone rings. Experiments conducted by us have definitely shown that they do not belong to the category of coumarins.

Under this group of substances whose constitutions are not yet definitely established may be included osagin and pomiferin which have been obtained from Osage orange peel. They are obtained as light yellow crystals having the formulae $C_{25}H_{24}O_5$ and $C_{25}H_{24}O_6$ respectively. They have marked reducing properties. They reduce Fehling's solution and produce silver mirror from Tollen's reagent and these are taken to be indications of ortho-dihydric phenol groupings. In a more recent publication by Wolfrom, Morgan and Benton²⁰ experimental data are given which suggest that osagin and the related compound pomiferin have flavone ring system in them. But it should be noted that in this case the hydroxyl groups are not methylated. This is in strange contrast to the complete methylation observed with the flavones in the Tangerine and the Chinese Manderine oranges.

Recently the peels of a variety of sweet orange (*citrus aurantium*) available in large quantities in the Vizagapatam district have been investigated. They are loose and hence are easily separated from the other parts of the fruits. The fresh peels are golden yellow in colour and when dried in the sun have a very pleasant aroma about them. By careful extraction, besides hesperidin, a pale yellow

crystalline compound melting at 123-24°C. has been isolated. It has the formula $C_{21}H_{22}O_8$. Since it is definitely different from others known to be present in citrus fruits it has been named Aurantin indicative of its origin from citrus aurantium. The free solid is not markedly bitter probably due to its sparing solubility in saliva, but in solution in very dilute alcohol it is distinctly bitter though the taste is not so strong as in the case of naringin and limonin. From the properties and reactions so far studied it seems to belong to the group of flavones.

REFERENCES

- ¹ Howell and Robertson, J., 1937, 294.
- ² Spath, Wesseley and Kubiczek, Ber., 1937, 478.
- ³ Bohme and Pietsch, Arch. Pharm., 1938, 482; Ber., 1939, 773 and 780.
- ⁴ Jois, Manjunath and Venkatarao, J.I.C.S., 1933, 41.
Seshadri and Venkatarao, Proc. Ind. Acad. Sci., A, 5, 351.
- ⁵ Rangaswami, Seshadri and Veeraraghaviah, Proc. Ind. Acad. Sci., A, 9, 328.
- ⁶ Bruckner and Szent-Gyorgyi, Nature, 1936, 138, 1057.
- ⁷ Yamamoto and Oshima, J. Agri. Chem. Soc. Japan, 1931, 7, 312.
- ⁸ Nelson, J.A.C.S., 1934, 1392.
- ⁹ Goldsworthy and Robinson, J., 1937, 46.
- ¹⁰ Neelakantam and Seshadri, Proc. Ind. Acad. Sci., A, 5, 357.
- ¹¹ Tseng, J.C.S., 1938, 1003.
- ¹² Robinson and Tseng, J.C.S., 1938, 1004.
- ¹³ Ratnagiriswaran, Sehra and Venkataraman, Bio. Chem. Jour., 1934, 1964.
- ¹⁴ Karrer and Venkataraman, Nature, 1935, 135, 878.
- ¹⁵ Bose *et al.*, J.I.C.S., 1938, 139; 1939, 183; 1940, 45.
- ¹⁶ Koller and Czarney, Montash, 1936, 67, 248; 1937, 70, 26.
- ¹⁷ Feist and Overberg, Ber., 1936, 69, 1322.
- ¹⁸ Seshadri and Veeraraghaviah, Proc. Ind. Acad. Sci., A, 11, 505.
- ¹⁹ Higby, J.A.C.S., 1938, 3014.
- ²⁰ Wolfrom, Morgan and Benton, J.A.C.S., 1940, 1482.

THE EVOLUTION OF ASEPTIC SURGERY

By

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The practice of surgery as an art dates from prehistoric times. By Papyrus Ebers and by Edwin Smith Papyrus a good deal of light is thrown on the scope and condition of surgery as practised in Egypt as early as 2000 B.C.—1700 B.C. A type of surgery more or less similar to the Egyptian was known in ancient China; and in so far as India is concerned, there are evidences indicating the practice of this art not only in the days of the *Atharva Veda*, but also in those of the *Rig Veda* of which 4000 B.C. forms the *terminus a quo*, and 1000 B.C. the *terminus ad quem*.





In Europe the foundations of scientific methods of medicine were laid by the Hippocratic School during 460 B.C.—370 B.C. Hippocrates wrote a surgical treatise, *On Injuries of the Head*; and the later Hippocratics developed considerable knowledge and skill in the profession. But in spite of all the progress made by the Hippocratic School, operations were extremely painful and dangerous in those days.

The practice of surgery remained in this unsatisfactory state until the latter half of the 19th century when it was revolutionized by the bacteriological discoveries of Louis Pasteur (1822–1895). Since the days of this French scientist, pyaemia and septicaemia which were so common have been rare, hospital gangrene, which was the scourge of every hospital after operation, has been unknown, and the bacteriological laboratory has been made an integral part of the equipment of a hospital for the diagnosis and cure of diseases.

In spite of all the aid derived by surgery from the bacteriological discoveries of Pasteur, the rate of fatality from major operations remained as high as 70 %. The state of affairs was, however, changed with the introduction of antiseptics by Joseph Lister (1827–1912). Thanks to the genius of this English surgeon, the present mortality of surgery hardly exceeds 3 %, and is more often

due to delay in undergoing an operation than to the operation itself. The use of antiseptics supplemented by the development of anaesthetics, on the one hand, and by the improved methods of operation

CHART SHOWING THE EVOLUTION OF ASEPTIC METHODS.

 KOCH 1843		 PASTEUR 1822	 LISTER 1827
1850.		STUDIES ON TARTARATES AND MOLECULAR ASYMETRY.	
		STUDIES ON FERMENTATION. CONTROVERSY ON SPONTANEOUS GENERATION.	SUPPURATION CAUSED BY BACTERIA ANTISEPTIC SURGERY.
1860		DISEASES OF WINE PEBRINE.	
1870	B. TYPHOSUS TRAUMATIC INFECTIONS.	DISEASES OF BEER. ANTHRAX STUDIES COMMENCED PAPER ON SERUM THEORY. CHICKEN CHOLERA & VACCINE	CARBOLIC SPRAY USED BY LORD LISTER.
1880	B. DIPHTHERIA. KLEB LOEFFLER BACILLUS.	VACCINATION AGAINST ANTHRAX RABIES TRANSMITTED TO DOGS. VACCINATION AGAINST RABIES. OPENING OF PASTEUR INSTITUTE.	DEVELOPMENT OF ASEPTIC METHODS BY BERGMANN AND SCHIMMELBUSCH.
1890		TUBERCULINE. 1895.	PUBLICATION OF SCHIMMELBUSCH.
1900		TYPHOID CARRIERS.	SPREAD OF ASEPTIC METHODS.
1910	1910		1912

After Lopley

and treatment, on the other, has made the modern hospital a home of cure with the minimum of pain and suffering in contrast with the pre-Listerian hospital which spelled death, agony and horror.

Furthermore, since the days of Lister, surgery has extended its beneficent sway from the extremities to all other regions of the body. Nowadays, every cavity or organ is fearlessly attacked by the surgeon's knife; the brain, the skull, the spine and the spinal cord, the eyes, the nose, the ears, the throat, and the lungs, which are the guardians of our life, are restored to their proper functions; the pleura is drained; parts of the diseased lobes of the lungs are removed; the thoracic cage is collapsed; the heart is sutured; the broken arteries and veins are anastomosed; the ovaries, the uterus, and the prostate are removed; the gall-bladder and the kidneys are opened or removed; the stomachs are opened and excised; and the intestines are repaired, resected, and anastomosed. Wide and successful operations are performed for cancer with relief and prolongation of life. The congenital or acquired deformities are restored to normality by plastic surgery, and the cripple problem is being solved. Compound fractures are turned into simple ones, and refractory bones are wired, plated, grafted and pegged. Joints are opened, cleaned, reconstructed, and transplanted, and thereby limbs are saved. Lives are saved by the transfusion of blood; and the grafting of organs like the testes, the ovaries, and the thyroid, is no longer considered to be an impracticable proposition.

The chart on the foregoing page which I have adapted from Topley by introducing therein (i) the photographs of three luminaries, namely Louis Pasteur, Joseph Lister, and Robert Koch, and (ii) the photograph of the carbolic spray used by Lister, indicates the main stages in the evolution of modern aseptic surgery which is not only an art, but also a science with marvellous achievements and infinite possibilities.

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ON SOME FUNDAMENTAL LIMITS IN ANALYSIS

By

V. RAMASWAMI

Introduction.—Perhaps the most fundamental limits, which form the basis of the differential calculus, are

$$(i) \lim_{x \rightarrow 1} \frac{x^m - 1}{x - 1}, \quad (ii) \lim_{x \rightarrow 0} \frac{a^x - 1}{x}, \quad (iii) \lim_{x \rightarrow 0} \frac{\sin x}{x}.$$

Of these the existence of the first for rational m follows rigorously from elementary considerations. The existing rigorous proofs of the existence of (i) for irrational m , and of (ii) and (iii) are based on definitions of a^x by means of the theory of inverse functions from a certain definite integral, and of a measure of angular magnitude by means of certain definite integrals (cf. Hardy: Pure Mathematics), or alternatively by means of the theory of infinite series and inverse functions. There seems to be no direct, rigorous treatment of these limits, which starts from direct definitions in conformity with the simple character of the intuitive notions of the tyro regarding the function a^x and angular magnitude. Such a treatment may be expected to have the advantage of introducing the fundamental constants e and π into analysis in a constructive fashion. This paper is the outcome of a desire to give a simple treatment on these lines. A general result, interesting in itself, comes in handy, and is stated and proved as a theorem. The existence of the limits in question follows immediately from this theorem and the theorem of the limit of a monotonic bounded function.

Definition of a^x for $a > 0$ and x real.—We define $a^0 = 1$, and regard $a^{\frac{1}{2}}$ as a positive number, uniquely determined from a by a construction or otherwise (e.g. Horner's process. Dedekind section, etc.) so as to satisfy the relation $a^{\frac{1}{2}} \cdot a^{\frac{1}{2}} = a$. We define $a^{\frac{1}{2^n}} = \left(a^{\frac{1}{2^{n-1}}}\right)^{\frac{1}{2}}$ for $n > 1$ and observe that $\left(a^{\frac{1}{2^n}}\right)^{2^n} = a$, and that $\lim_{n \rightarrow \infty} a^{\frac{1}{2^n}} = 1$. Now

any real number x can be represented uniquely in the form

$$m + \frac{a_1}{2} + \frac{a_2}{2^2} + \dots + \frac{a_n}{2^n} + \dots$$

where m is an integer (positive, negative, or zero), $a_n = 0$, or 1 for every n , and an infinity of the a_n 's are equal to 1. We define a^x as the limit of the monotonic bounded sequence b_n where

$$b_n = a^m \cdot a^{\frac{a_1}{2}} \cdot a^{\frac{a_2}{2^2}} \dots a^{\frac{a_n}{2^n}}.$$

Remarks.—From the definition follow immediately for $a > 0$:—
 $a^0 = 1$; $a^\delta \geq 1$ for $a \geq 1$ and $\delta > 0$; a^x is a strictly monotonic function of x for $a \neq 1$, and equal to 1 for every x if $a = 1$; $\lim_{x \rightarrow 0} a^x = 1$;

$$a^{x_1} \cdot a^{x_2} = a^{x_1 + x_2}; a^{x_1 x_2} = (a^{x_1})^{x_2}, a^x \cdot b^x = (ab)^x \text{ for } a > 0, b > 0.$$

Definition of a measure of angular magnitude.—We assign 0 to the null angle, viz., the angle between two coincident rays; and assign 1 to the right angle. We observe that $\frac{1}{2^n}$ of the right angle can be constructed by repeated bisection of the right angle and that the sine of this angle tends to 0 as $n \rightarrow \infty$. We assign $\frac{a_1}{2} + \frac{a_2}{2^2} \dots + \frac{a_n}{2^n}$ where $a_n = 0$ or 1 to the angle that can be formed by the addition of the corresponding parts of the right angle. To any angle \hat{A} less than a right angle, we observe, that there corresponds a unique sequence of a_n 's taking values 0 or 1, and such that
 angle $\left(\frac{a_1}{2} + \frac{a_2}{2^2} \dots + \frac{a_n}{2^n}\right) < \text{angle } \hat{A} \leq \text{angle} \left(\frac{a_1}{2} + \frac{a_2}{2^2} \dots + \frac{a_n}{2^n} + \frac{1}{2^n}\right).$

We assign to the angle \hat{A} the number $\alpha = \frac{a_1}{2} + \frac{a_2}{2^2} \dots + \frac{a_n}{2^n} \text{ ad. inf.}$

and note that (1) $\sin \alpha = \sin \hat{A} = \lim_{n \rightarrow \infty} \sin \text{angle} \left(\frac{a_1}{2} + \frac{a_2}{2^2} \dots + \frac{a_n}{2^n}\right).$

Given any number $\alpha = \frac{a_1}{2} + \frac{a_2}{2^2} + \dots + \frac{a_n}{2^n} + \text{ad. inf.}$ where $a_n = 0$,

1 for every n , we construct the angle \hat{A} such that the second equality in (1) is satisfied. It is then easily seen that the measure of \hat{A} as

above defined is precisely α . It is also obvious that as α strictly increases from 0 to 1, $\sin \alpha$ strictly increases from 0 to 1 and takes all values in between.

(Note.—The fundamental (geometric) property that the sine increases strictly as the angle increases from null to the right angle is the basis of this and the other definitions referred to in the introduction.)

Theorem: Let $f(x)$ be a real function, continuous or monotonic in $(0 \leq x \leq a)$, and such that

$$(2) \quad f(x_1) + f(x_2) > 2f\left(\frac{x_1 + x_2}{2}\right) \text{ for } 0 \leq x_1 < x_2 \leq a.$$

Let x_1, x_2, \dots, x_n be numbers not all equal in the closed interval $(0, a)$, and $0 < m < 1$. Then

$$(3) \quad f(x_1) + f(x_2) + \dots + f(x_n) > nf\left(\frac{x_1 + x_2 + \dots + x_n}{n}\right);$$

and

$$(4) \quad m(f(x) - f(0)) > f(mx) - f(0) \text{ for } 0 < x \leq a.$$

$$(5) \quad \text{The Theorem is true with } \geq \text{ throughout instead of } >.$$

Proof.—(3) follows from (2) by a method, *mutatis mutandis*, employed to prove the theorem of the arithmetic and the geometric mean in Hardy, Littlewood, and Polya: Inequalities. Let now $0 < p < n$ where p and n are integers and $\alpha = \frac{p}{n}$. Putting $x_1 = x_2 = \dots = x_p = x$ and $x_{p+1} = \dots = x_n = 0$ in (3) we get

$$\alpha f(x) + (1 - \alpha) f(0) > f(\alpha x) \text{ for } 0 < x \leq a,$$

$$(4.1), \text{ i.e. } \alpha(f(x) - f(0)) > f(\alpha x) - f(0) \text{ for } 0 < x \leq a,$$

and α rational and $0 < \alpha < 1$.

Let now β be irrational and $0 < \beta < 1$ and $\varepsilon > 0$. Then, since $f(x)$ is either continuous or monotonic, we can find a rational number α between 0 and 1 such that

$$(4.2) \quad f(\alpha x) > f(\beta x) - \frac{\varepsilon}{2}, \text{ and } |\beta - \alpha| |f(x) - f(0)| < \frac{\varepsilon}{2}.$$

Then we have

$$\begin{aligned}\beta(f(x)-f(0)) &= \alpha(f(x)-f(0)) + (\beta-\alpha)(f(x)-f(0)) \\ &> f(\alpha x)-f(0) + (\beta-\alpha)(f(x)-f(0)), \text{ by (4.1),} \\ &\geq f(\alpha x)-f(0) - |\beta-\alpha| |f(x)-f(0)|, \\ &> f(\beta x)-f(0)-\varepsilon, \text{ by (4.2).}\end{aligned}$$

Hence,

$$(4.3) \quad \beta(f(x)-f(0)) \geq f(\beta x)-f(0) \text{ for } 0 < x \leq a; \beta \text{ irrational and } 0 < \beta < 1.$$

Now the m of the theorem can always be expressed in the form $m = \alpha\beta$ where α is rational and $0 < \alpha, \beta < 1$. Then follows by (4.1) and (4.3),

$$\begin{aligned}m(f(x)-f(0)) &= \beta\alpha (f(x)-f(0)) > \beta(f(\alpha x)-f(0)) \geq f(\beta\alpha x)-f(0) \\ &= f(mx)-f(0).\end{aligned}$$

This proves (4); and (5) is now obvious.

Corollaries.—(A). For $a > 0$ and $a \neq 1$, $\frac{a^x-1}{x}$ and $\frac{a^{-x}-1}{x}$ are both strictly increasing functions of x for $x > 0$; further for $0 < |x| < 1$, we have

$$1 - \frac{1}{a} < \frac{a^x-1}{x} < a-1.$$

$$(B). \quad \lim_{x \rightarrow 0} a^x = 1; (a > 0).$$

$$(C). \quad \text{For } a > 1, \frac{a^x-a^{-x}}{x} \text{ is a strictly increasing function of } x \text{ for}$$

$$x > 0 \text{ and } \lim_{x \rightarrow 0} \frac{a^x-a^{-x}}{x} \text{ exists and is not negative.}$$

$$(D). \quad \text{The functions } \frac{-\sin x}{x}, \frac{\tan x}{x} \text{ are both strictly increasing}$$

for $0 < x < 1$ with the measure defined above.

Proof.—We observe that the functions $a^x, a^{-x}, a^x-a^{-x}, -\sin x, \tan x$ satisfy the condition (2) in the ranges stated. The results then follow from (4) and the theorem of the limit of a monotonic bounded function.

The limit (i) :

Let n be an integer greater than $|m-1|$.

By corollary (A) we have for $x>0$ and $x\neq 1$

$$mx^{m-1}(x-1) \leq x^{m-1} \leq m(x-1)$$

Hence,

$$\begin{aligned} |x^{m-1} - m(x-1)| &\leq |m(x^{m-1}-1)(x-1)|, \\ \left| \frac{x^m-1}{x-1} - m \right| &\leq |m| |x^{m-1}-1| \leq |m| |x^{m-1}-x^{-(m-1)}| \\ &\leq |m| |x^n-x^{-n}| \rightarrow 0 \text{ as } x \rightarrow 1. \end{aligned}$$

Hence,

$$\lim_{x \rightarrow 1} \frac{x^m-1}{x-1} = m, \text{ (} m \text{ any real number).}$$

The limit (ii) :

We have, for $a>0$,

$$\frac{a^x-1}{x} = \frac{a^{\frac{x}{2}}}{2} \cdot \frac{a^{\frac{x}{2}}-a^{-\frac{x}{2}}}{\frac{x}{2}} \rightarrow \frac{1}{2} \lim_{x \rightarrow 0} \frac{a^x-a^{-x}}{x}$$

by corollaries (B) and (C).

Note.—If this limit be denoted by $l(a)$, say, then

$$1 - \frac{1}{a} < l(a) < a-1 \text{ for } a \neq 1, \text{ and } a > 0$$

by corollary (A); and it is easy to show that $l(a^x) = xl(a)$ and hence that $a = e^{l(a)}$ where $e = \lim_{x \rightarrow 0} (1+x)^{\frac{1}{x}}$; thus introducing the number e and the 'natural' logarithm.

The limit (iii) (with the angular measure above defined).

Obviously we have, for $0 < x < 1$,

$$0 < \frac{\sin x}{x} < \frac{\tan x}{x},$$

and $\frac{\sin x}{x}$ strictly increases while $\frac{\tan x}{x}$ strictly decreases as $x \rightarrow +0$, by corollary (D).

Hence for $0 < x < y < \frac{1}{2}$, we have

$$1 < \frac{\sin y}{y} < \frac{\sin x}{x} < 2 \tan \frac{1}{2} = 2.$$

Hence $\lim_{x \rightarrow +0} \frac{\sin x}{x}$ exists as the limit of a monotonic bounded function, and lies between 1 and 2.

Note.—If this limit be α , and we assign αx to the angle with measure number x in the above defined system, we have, with this new system of measure which is obviously additive

$$\lim_{x \rightarrow +0} \frac{\sin x}{x} = 1$$

and $\lim_{x \rightarrow 0} \frac{\sin x}{x} = 1$, since $\frac{\sin x}{x}$ is an even function of x . The measure of two right angles in this new system suggests itself now as a number of obvious importance, and thus the number π is introduced.

AN AFFINE EXTENSION OF LIOUVILLE'S THEOREM

By

K. NAGABHUSHANAM

Lagrange's equations of motion in terms of generalized co-ordinates $(q_1, q_2, \dots q_n)$ equal in number to the degrees of freedom of a conservative holonomic dynamical system in a form free from the unknown reactions constitute a remarkable recasting of Newton's equations of motion. While Lagrange's differential equations of motion are n in number and of the second order, Hamilton transformed them into $2n$ partial differential equations of the first order in terms of the n q 's and their n conjugate momenta $(p_1, p_2, \dots p_n)$. These equations in turn yield the theorem of Liouville¹ that

$$\frac{D\tau}{Dt} = \frac{\partial\tau}{\partial t} + \sum_1^n \left\{ \frac{\partial\tau}{\partial q^s} \dot{q}^s + \frac{\partial\tau}{\partial p_s} \dot{p}_s \right\} = 0,$$

where τ stands for the density of representative points.

We can interpret this geometrically² in the manifold of states S_{2n} of variables $(q_1, \dots q_n, p_1, \dots p_n)$, treated as a system of orthogonal cartesian co-ordinates, as the even distribution without crowding of the trajectories in space.

It is the object of the present paper to examine whether in the light of modern geometrical ideas it is not possible to give an invariantive affine geometrical formulation to this theorem of Liouville.

Geometrization of dynamics was practically started by Hamilton by his studies in contact transformations and the Characteristic function. Subsequently not only have geometrical interpretations been sought, but also new types of geometries have been created to serve as suitable pictures of nature. To-day this line of work is at its height, and recently E. A. Milne³ in his presidential address to the London Mathematical Society has suggested that there is no essential difference between geometrical theorems and laws of nature. Numerous types of geometries⁴ have been considered by various workers to give a geometrical formulation to their ideas. Levi-civita's

interpretation of parallel transport has led the way to the generalization of the Riemannian geodesics to the non-Riemannian autoparallels by seeking solutions for the coefficients of connection which are not necessarily related to a symmetric covariant tensor of the second order as Christoffel symbols of the second kind are related to the metrical groundform. In this geometry all the notions are based on parallelism without any idea of the metric of distance and angle. If the coefficients of connection are such that

$$\Gamma_{jk}^i = \Gamma_{kj}^i,$$

the geometry is called affine geometry. A theorem in affine space is also true in Riemannian space, but the converse is not necessarily true. As such, it becomes essential for clear understanding to examine which of the known results are true in general affine space and which others necessarily involve the ideas of metric. In one such inquiry it was found by the author⁵ that the generalization of the converse of the theorem

$$\text{div. curl } A = 0$$

holds good in general affine space.

Let us now consider the manifold of States and Time S_{2n+1} of the variables $(q_1, \dots, q_n, p_1, \dots, p_n, t)$. To a motion of the dynamical system in the ordinary 3-space of our experience there corresponds a trajectory of the representative point in S_{2n+1} . Liouville's theorem implies the notion of the measure of the volume in S_{2n} . In the enveloping S_{2n+1} it is here shown that the vanishing of the divergence of a vector density codirectional with the trajectories is the affine equivalent.

In what follows the notation of tensor calculus with the summation convention will be adopted. The equations of the trajectories in variables $(x^1, x^2, \dots, x^{2n+1})$ in S_{2n+1} are given by

$$a_{ik} dx^k = 0, \quad (i, k = 1, \dots, 2n+1) \quad \dots \quad (1)$$

where

$$a_{ik} = \frac{\partial X_i}{\partial x^k} - \frac{\partial X_k}{\partial x^i},$$

and the rank of the matrix

$$|a_{ik}; X_k| \text{ is } 2n+1.$$

If (A^{ik}) are the cofactors of a_{ik} in the determinant $|a_{ik}|$, they form a contravariant tensor of weight two and order two. By the theory of the skew-symmetric determinant of odd order we have ⁶

$$A^{ik} = \alpha^i \alpha^k,$$

where (α^i) is a vector density. Equations (1) constitute the Pfaff's first system for the linear differential form $X_i dx^i$, and hence form a completely integrable system ⁷. If we choose variables y_1, y_2, \dots, y_{2n} as $2n$ independent integrals of (1) and y_{2n+1} independent of them, in these variables which may be called Integrals-co-ordinates

$$a_{i(2n+1)} = 0^8, (i = 1, 2 \dots 2n+1),$$

and the only non-vanishing A^{ik} is

$$(\alpha^{(2n+1)})^2 = A^{(2n+1)(2n+1)} = 1.$$

Hence

$$\alpha^{2n+1} = \pm 1.$$

Therefore

$$\frac{\partial \alpha^{2n+1}}{\partial y^{2n+1}} = 0.$$

Also $\frac{\partial \alpha^j}{\partial y^j} = 0$, ($j = 1, 2 \dots 2n$), for every α^j is a constant, viz. zero.

Thus

$$\frac{\partial \alpha^i}{\partial y^i} = 0, \quad \dots \quad \dots \quad \dots \quad (2)$$

(with the summation convention for i from 1 to $2n+1$).

If in this co-ordinate system of the y 's, the coefficients of connection are taken as

$$\Gamma_{jj}^j = f_j(y) \quad (j = 1, 2 \dots 2n)$$

without the summation for the repeated j , and all other coefficients zero, the trajectories become the transversals of parallelism for the $2n$ vector fields given by the parametric lines of y^1, y^2, \dots, y^{2n} . It is of interest to note that for all systems of co-ordinates (z^i) connected with (y^i) by the transformations of the type

$$Z^j = a_p^j y^p \quad (j, p = 1, 2 \dots 2n) \\ Z^{2n+1} = \Phi(y^{2n+1}),$$

where (a_p^j) are constants,

the equations of transformation of the coefficients of connection retain the group property of being in the form

$$\overline{\Gamma}_{jj}^j = \varphi_j(z), \quad (j = 1, 2, \dots 2n)$$

without the summation for the repeated index j , and all other coefficients being zero.

In space so connected the equation (2) is tensor-invariant, for

$$\operatorname{div} \alpha^i = \operatorname{div} \sqrt{A^{ii}} = \alpha_{,i}^i = \frac{\partial \alpha^i}{\partial y^i} = 0,$$

where the comma denotes covariant differentiation with respect to the connection. Thus (α^i) is the required contravariant vector density codirectional with the trajectories and with a vanishing divergence. The result of this paper may now be stated as

Theorem:

In affine manifold of States and Time the divergence of the vector density codirectional with the trajectories formed by the square-roots of the cofactors of the diagonal elements of the determinant of the coefficients of the bi-linear covariant of the action form $X_i dx^i$ of class $2n+1$ is zero, i.e.,

$$(\sqrt{A^{ii}}), i = 0.$$

As corollary to this result we get

(i) $\sqrt{A^{ii}} \varepsilon_{\alpha_1 \dots \alpha_{2n} i}$ is a Stokes tensor, where $(\varepsilon_{\alpha_1 \dots \alpha_n})$ is the familiar numerical tensor of weight -1 ,

$$(ii) \iint \dots \int X_i \sqrt{A^{ii}} dx^1 dx^2 \dots dx^{2n+1}$$

is an integral invariant of order $2n+1$ attached to the trajectories, and

$$(iii) \iint \dots \int \left[\frac{\sqrt{A^{11}} dx^2 \dots dx^{2n+1} - \sqrt{A^{22}} dx^1 dx^3 \dots}{dx^{2n+1} + \dots - \dots + \sqrt{A^{(2n+1)(2n+1)}} dx^1 \dots dx^{2n}} \right]$$

is an integral invariant of order $2n$ obtained from the previous one by Goursat's E-operation⁹. In the (q, p, t) variables these take the familiar forms¹⁰.

REFERENCES

- ¹ Jeans: *Dynamical Theory of Gases*, 4th ed., p. 73.
- ² Jeans: *Ibid.*, p. 73.
- ³ *Journal London Math. Soc.*, Vol. 15, Part I, No. 57, pp. 48-49.
- ⁴ For a comprehensive list of papers see B. S. Madhava Rao: *Generalized Geometry and Physical Theories*, Math. Student, (1940), Vol. 8, No. 1, pp. 32-34.
- ⁵ K. Nagabhushanam: *Journal London Math. Soc.*, Vol. 9, Part 1, pp. 13-15.
- ⁶ G. Kowalewski: *Determinanten-theorie*, p. 124.
- ⁷ E. Goursat: *Leçons sur le problème de Pfaff*, p. 27.
- ⁸ K. Nagabhushanam: *Transformation Theory of Dynamics*, *Journal Indian Math. Soc.*, Vol. 20, p. 241.
- ⁹ E. Goursat: *Ibid.*, p. 243.
- ¹⁰ K. Nagabhushanam: *On a Property of the Lagrangian*, *Journal Indian Math. Soc.*, New Series, Vol. 4, No. 3, pp. 89-90.

GENERALISATIONS OF A THEOREM OF ESTERMANN IN THE ADDITIVE PRIME NUMBER THEORY

By

K. SAMBASIVA RAO

Introduction

One of the greatest discoveries in Mathematics in recent times is the proof by Vinogradoff¹ that every sufficiently large odd number is expressible as the sum of three odd primes. Estermann² proved a somewhat similar result, viz., that every sufficiently large odd number n is expressible in the form

$$n = p_1 + p_2 + p_3 p_4$$

where the p 's denote odd primes. Walfisz³ subsequently gave an alternative proof of the above theorem of Estermann.

The purpose of the present paper is to prove results which are of a more general character than that of Estermann.

In what follows p always denotes an odd prime and $F_1(x)$, $F_2(x)$, \dots , $F_r(x)$ ($r \geq 1$) denote integral valued polynomials whose first coefficients b_{10} , b_{20} , \dots , b_{r0} are all positive. Let the degree of the last polynomial be k . For the sake of definiteness we shall suppose that $F_1(1) F_2(1) \dots F_r(1)$ is odd.

Theorem 1: Every sufficiently large odd number n is representable in the form

$$n = p_1 + p_2 + F_1(p_3) F_2(p_4) \dots F_r(p_{r+2}).$$

To the same category belong the following theorems.

Theorem 2: Let (A) denote the set of residue classes (mod. 24) in

$$4 + F_1(x) F_2(x) \dots F_r(x_r), (x_s, 24) = 1, s = 1, \dots, r.$$

Then every sufficiently large integer x is representable in the form

$$n = p_1^2 + p_2^2 + p_3^2 + p_4^2 + F_1(p_5) F_2(p_6) \dots F_r(p_{r+4}),$$

when n belongs to one of the residue classes (A).

Theorem 3: Every sufficiently large odd number n is expressible in the form

$$n = p_1^3 + p_2^3 + \dots + p_8^3 + F_1(p_9)F_2(p_{10}) \dots F_r(p_{r+8}).$$

Theorem 4: Let (B) denote the set of residue classes (mod. 240) in

$$14 + F_1(x_1)F_2(x_2) \dots F_r(x_r), (x_s, 24) = 1, s = 1, \dots, r.$$

Then every sufficiently large integer n belonging to one of the residue classes (B) is representable in the form

$$n = p_1^4 + p_2^4 + \dots + p_{14}^4 + F_1(p_{15}) \dots F_r(p_{r+14}).$$

Theorem 5: Every sufficiently large odd integer n is representable in the form

$$n = p_1^5 + p_2^5 + \dots + p_{24}^5 + F_1(p_{25})F_2(p_{26}) \dots F_r(p_{r+24}).$$

Similar theorems can be stated for higher powers. The proofs of the above theorems are similar to that of theorem 5, which when given completely extends to considerable length. Considerations of space force me to give a very brief indication of the lines of proof of theorem 5. The complete details of the proof will appear elsewhere.

1. Notation

In what follows all small latin letters except e and c denote positive integers. δ is a fixed sufficiently small positive number and ε is an arbitrarily small positive number. N is a sufficiently large odd number. $P = \frac{1}{2}N^{\frac{1}{2}}$. $L = \log N$. c, c_1, c_2, \dots and h, h_0, h_1, \dots are (sufficiently large) positive constants independent of N . v denotes a typical number representable in the form

$$v = p_1^5 + p_2^5 + \dots + p_7^5.$$

$$T(\alpha) = \sum_{x \geq P}^{2P} e(ax^5); \quad e(x) = e^{2\pi i x}$$

$$S(\alpha) = \sum_{p \geq P}^{2P} e(ap^5)$$

$$V(\alpha) = \sum_{v \geq P^{\alpha} + \nu} e(\alpha v)$$

where

$$\nu = \frac{9,604}{147,269}.$$

$$f_1(\theta, L) = \sum_{p_{25} \leq L} e(\theta F_1(p)),$$

$$f_2(\theta, L) = \sum_{p_{26} \leq L} f_1(\theta F_2(p), L).$$

$$\begin{array}{cccccccccccc} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array}$$

$$f_{r-1}(\theta, L) = \sum_{p_{23+r} \leq L} f_{r-2}(\theta F_{r-1}(p), L),$$

$$f_r(\theta) = \sum_{p_{24+r}} f_{r-1}(\theta F_r(p), L),$$

$$F_r(p) \leq N/L^c$$

where c is so chosen that

$$F_1(p_{25}) \cdot F_2(p_{26}) \dots F_r(p_{24+r}) \leq \frac{1}{4} N$$

when p_{25}, \dots, p_{24+r} lie in their respective ranges.

$$Q = (N/b_{ro}L^c)^{\frac{1}{k}}$$

$$J(z) = \int_P^{2P} \frac{e^{2\pi i x^5 z}}{\log x} dx; \quad I(z) = \frac{5}{L} \int_P^{2P} e^{2\pi i x^5} dx.$$

$T = PL^{-h}$. $A \ll B$ means that $A = O(B)$. $q, = \varphi(q)$, the well-known Euler's totient function.

$$W_{t,q} = \sum_{\substack{l=1 \\ (l,q)=1}}^q l_q(tl^5); \quad l_q(x) = e^{2\pi i x/q}$$

$$B(N, q) = \sum_{\substack{t=1 \\ (t,q)=1}}^{\frac{q}{2}} \left(\frac{W_{t,q}}{q_1} \right)^{10} l_q(-tN).$$

$S(N, R) = \sum_{q=1}^R B(N, q)$; $S(N) = S(N, \infty)$. This is called the singular series. This $S(N)$ may not be confused with $S(\alpha)$.

2. The Singular Series

Lemma 1 :

$$W_{i,q} = 0 \ (q^{\frac{1}{2}+\epsilon}).$$

Lemma 2 :

$$S(N) - S(N, R) = O(R^{-s+\epsilon}).$$

Lemma 3 :

$$S(N) \geq c_1 < 0$$

where c_1 is independent of N .

The above lemmas can be proved by the usual argument. See, for example, Hua ⁴.

3. The Farey Dissection

If we prove that

$$I(N) = \int_{-\frac{1}{\tau}}^{1-\frac{1}{\tau}} S^{10}(\alpha) V^2(\alpha) f_r(\alpha) e^{-2\pi i \alpha N} d\alpha > 0$$

we shall be proving the theorem. Every α of the interval of integration can be put in the form

$$\alpha = \frac{a}{q} + \frac{\theta}{q\tau}; \quad \frac{1}{2} \leq |\theta| \leq 1, \ (a, q) = 1, \ 0 < q \leq T.$$

If α is representable in the form

$$\alpha = \frac{a}{q} + \beta; \quad -\frac{1}{\tau} < \beta \leq \frac{1}{\tau}, \ 0 < q \leq L^h$$

we say that α belongs to a major arc, otherwise we say that it belongs to a minor arc. Every α on a minor arc can be put in the form

$$\alpha = \frac{a}{q} + \frac{\theta}{q\tau}; \quad (a, q) = 1, \ L^h < q \leq \tau.$$

Further it is easily seen that no two major arcs overlap with one another. Corresponding to the division of the interval of integra-

tion into major and minor arcs $I(N)$ can be divided into parts $I_1(N)$ and $I_2(N)$. Thus we have

$$I(N) = I_1(N) + I_2(N).$$

4. Minor Arcs

Lemma 6: Let v_1, v_2, \dots, v_v be a set of integers such that

$$v_v \leq P^{4+\mu} \quad (0 < \mu < \tfrac{1}{4})$$

and

$$V > c_2 P^{4-7\mu} \quad \dots \quad \dots \quad \dots \quad (1)$$

then the number of solutions of

$$x^5 + v_h = y^5 + v_j \quad \dots \quad \dots \quad \dots \quad (2)$$

subject to

$$P \leq x, y \leq 2P \quad \dots \quad \dots \quad \dots \quad (3)$$

is

$$O(P^2 V^2 P^{-5+7\mu+\epsilon}) \quad \dots \quad \dots \quad \dots \quad (4)$$

This lemma and the next one are proved by extending the principles of lemmas 1 and 2 in Davenport⁵.

Lemma 7: Let γ_s ($s \geq 2$) be a number such that the number $H_s(N)$ of integers less than N that are expressible in the form

$$n = p_1^5 + \dots + p_s^5$$

is greater than $c_3 N^{\gamma_s - \epsilon}$. Then

$$\gamma_2 = \frac{2}{5}, \gamma_3 = \frac{19}{35}, \gamma_4 = \frac{1}{5} \cdot \frac{109}{33}, \gamma_5 = \frac{297}{5 \cdot 79}, \gamma_6 = \frac{1}{5} \cdot \frac{6,283}{1,531}.$$

$$\gamma_7 = \frac{1}{5} \cdot \frac{65,231}{14,967}, \gamma_8 = \frac{669,117}{147,519}, \dots, \gamma_s = \frac{7+33\gamma_{s-1}}{35+5\gamma_{s-1}}.$$

Lemma 8:

$$\int_0^1 |S^{10}(\alpha) V^2(\alpha)| d\alpha = O(P^5 V^2 L).$$

Proof:—It is easily seen that

$$\int_0^1 |S^{10}(\alpha) V^2(\alpha)| d\alpha \leq \int_0^1 |T^{10}(\alpha) V^2(\alpha)| d\alpha.$$

Hence it is sufficient if we prove that

$$\int_0^1 |T^{10}(\alpha)V^2(\alpha)| d\alpha = O(P^5V^2L) \quad \dots \quad (5)$$

To prove this, as usual we divide the interval of integration into arcs corresponding to the Farey fractions t/q of order $P^{4+\delta}$. Those arcs for which $q < P^{1-\delta}$ we call the major arcs and the remaining arcs the minor arcs. Every α is therefore put in the form

$$\alpha = \frac{a}{q} + \beta \quad \text{where} \quad |\beta| \leq q^{-1}P^{-(4+\delta)}.$$

For $q \leq P^{1-\delta}$ and $\beta = O(q^{-1}P^{-4-\delta})$ we have (see, for example, lemma 9 of Davenport⁵),

$$T(\alpha) = O(q^{-\frac{1}{2}} \min(P, P^{-4}|\beta|^{-1})).$$

Hence integrating on the major arcs we have

$$\begin{aligned} & \sum_M \int_M |T(\alpha)|^2 |V(\alpha)|^2 d\alpha \\ &= O(V^2 \sum_M \int_M q^{-2} \min(P^{10}, P^{-40}|\beta|^{-10}) d\beta) \\ &= O(V^2 \sum_{q \leq P^{1-\delta}} \sum_a q^{-2} \int_0^\infty (P^{10}, P^{-40}|\beta|^{-10}) d\beta) \\ &= O(V^2 P^5 L) \quad \dots \quad (6) \end{aligned}$$

For $P^{1-\delta} < q \leq P^{4+\delta}$ and $\beta = O(q^{-1}P^{-4-\delta})$ we have, by using Weyl's inequality (see, for example, lemma 11 of Davenport⁵),

$$T(\alpha) = O(P^{1-\frac{1}{18}+\delta}).$$

Hence integration on the minor arcs gives

$$\begin{aligned} \sum_m \int_m |T^{10}(\alpha)| |V^2(\alpha)| d\alpha &= O(P^{8-\frac{1}{2}+8\delta} \int_0^1 |T^2(\alpha)| |V^2(\alpha)|^2 d\alpha) \\ &= O(P^{8-\frac{1}{2}+8\delta} P^2 V^2 P^{-5+7\mu+\epsilon}) \\ &= O(P^5 V^2) \quad \dots \quad \text{by lemma 6,} \quad (7) \end{aligned}$$

Hence the lemma follows from (5), (6) and (7).

Lemma 9: Let k be an integer, $0 < k \leq L^{hk}$;

$$S = \sum_{p \leq N_0} e^{\epsilon \pi i k f(p)}; \quad f(x) = \alpha x^n + \alpha_1 x^{n-1} + \dots + \alpha_n;$$

$$\alpha, \alpha_1, \dots, \alpha_n \text{ real}; \quad \alpha = \frac{a}{q} + \frac{\theta}{q\tau}, \quad (\alpha, q) = 1, \quad L^{hk} < q < \tau.$$

For arbitrary h_0 and $h \geq h$ where

$h_4 = \max((2n+1)[2h_k + 2^{2n+1}(h_0+2)+1]; (2n+1)(2^{2n-2}+1))$
we have the inequality

$$S \ll N_0 L^{-h_0}$$

This is satz 1 in Vinogradoff⁶.

Lemma 10: On the minor arcs we have

$$f_r\left(\alpha, \frac{N}{L^c}\right) = O(Q/L^{h_1})$$

where h_1 can be made as large as we please by a proper choice of our original h .

This follows easily from the previous lemma with

$$k = F_1(p_{25}) \dots F_{r-1}(p_{23+r}) \text{ and } n = k.$$

Lemma 11: On the minor arcs we have

$$I_2(N) = O(QP^5V^2L^{-h_2})$$

where h_2 can be chosen as large as we please by a proper choice of h_1 (according to lemma 10).

Proof:—

$$\sum_m \int_m S^{10}(\alpha) V^2(\alpha) f_r(\alpha) e^{-2\pi i \alpha N} d\alpha$$

$$\ll \frac{Q}{L^{h_1}} \int_0^1 |S^{10}(\alpha) V^2(\alpha)| d\alpha$$

by lemma 10,

$$\ll \frac{Q}{L^{h_1}} P^5 V^2 L$$

by lemma 8,

$$\ll P^5 V^2 Q L^{-h_2}.$$

5. Major Arcs

Lemma 12: If α is on a major arc

$$S(\alpha) = \frac{W_{l,q}}{q_1} J(\beta) + O(PL^{-h_3})$$

where h_3 can be chosen sufficiently large. For proof see 3°, page 52, Vinogradoff⁶.

Lemma 13:

$$J(\beta) \ll Z$$

where $Z = \begin{cases} PL^{-1} & \text{for } |\beta| \leq N^{-1} \\ L^{-1} |\beta|^{-\frac{1}{2}} & \text{for } N^{-1} \leq |\beta| \leq T^{-1} \end{cases}$

The lemma follows by the change of variable of integration.

Lemma 14: Let Q_{aq} denote the part of the integral

$$\int_{-\frac{1}{\tau}}^{1-\frac{1}{\tau}} S^{10}(\alpha) e^{-2\pi i \alpha N} d\alpha; \quad N \ll N_1 \ll N,$$

corresponding to the farey arc $\frac{a}{q}$ ($0 < q \leq L^h$) and R the integral

$$\int_{-\frac{1}{\tau}}^{\frac{1}{\tau}} [J(B)]^{10} e^{-2\pi i \beta N_1} d\beta.$$

Then

$$Q_{aq} = \left(\frac{W_{aq}}{q_1} \right)^{10} e^{-2\pi i \frac{a}{q} N_1} R + O(q_1^{-1} P^5 L^{-6-h_5})$$

where h_5 can be chosen as large as we please.

Proof:—Section 5°, Vinogradoff⁶ with $r = 5$.

Lemma 15:

$$R = L^{-10} \cdot P^5 \cdot K + O(P^5 L^{-11} \log L); \quad K > C > 0.$$

Proof:—Section 6°, Vinogradoff⁶ with $r = 10$, $N_0 = P$, $n = 5$.

Lemma 16:

$$\sum_{q=1}^{L^h} \sum_{\substack{a=1 \\ (a,q)=1}}^q Q_{aq} = S(N_1, L^h) L^{-10} P^5 K + O(P^5 L^{-11} \log L) > C_4 L^{-10} P^5 K.$$

Proof:—This easily follows from lemmas 15 and 14 by summing both sides of the equation in lemma 14 with respect to a and q . The latter part follows from lemma 3.

6. Concluding Argument

Lemma 17:

$$I(N) > C_5 Q P^5 L^{-11+r} V^2 / \log Q.$$

Proof:—

$$\begin{aligned} I(N) &= \int_{-\frac{1}{\tau}}^{1-\frac{1}{\tau}} S^{10}(\alpha) V^2(\alpha) f_r(\alpha) e^{-2\pi i \alpha N} d\alpha \\ &= \int_{-\frac{1}{\tau}}^{1-\frac{1}{\tau}} S^{10}(\alpha) \sum_{v, v^1, p_{25}, \dots, p_{r+24}} e^{2\pi i \alpha (v + v^1 + F_1(p_{25}) \dots F_r(p_{r+24}))} e^{-2\pi i \alpha N} d\alpha \\ &= \sum_{v, v^1, p_{25}, \dots} \int_{-\frac{1}{\tau}}^{1-\frac{1}{\tau}} S^{10}(\alpha) e^{-2\pi i \alpha N_1} d\alpha \end{aligned}$$

where

$$N_1 = N - v - v^1 - F_1(p_{25}) \dots F_r(p_{r+24}).$$

But $N > N_1 > N/4$ by our choice of the ranges for the variables.

It is easy to see that if we perform the integration over all the major arcs we get $I_1(N)$ and over all minor arcs we get $I_2(N)$. $I_2(N)$ has been dealt with before.

By lemmas 16, 2 and 5 we have

$$\begin{aligned} I_1(N) &= \sum_{v, v^1, p_{25}, \dots} \sum_{q=1}^{L^h} \sum_{\substack{a=1 \\ (a, q)=1}}^q Q_{aq} \\ &> \sum_{v, v^1, p_{25}, \dots} C_4 P^5 L^{-10} \end{aligned}$$

by lemma 16

$$> C_6 L^{-11+r} P^5 V^2 Q / \log Q.$$

But by lemma 11

$$I_2(N) < C_7 P^5 V^2 Q L^{-h_2}.$$

Hence lemma 17 and consequently the theorem are proved.

REFERENCES

- ¹ Vinogradoff: 'Representation of an odd number as a sum of three primes.' C. R. Acad. Sci., URSS, 15 (1937), 169-72.
- ² Estermann: 'A new result in the Additive Prime-number Theory.' Quart. Jour. of Maths., Vol. 8, (1937), 32-38.
- ³ Walfisz: 'Zur additive Zahlentheorie IV.' Trav. Inst. Math. de Tbilissi, 3 (1938), 121-189.
- ⁴ Hua: 'Representation of numbers as sums of powers of primes.' Math. Zeitschrift, 44 (1938), 335-46.
- ⁵ Davenport: 'On Waring's Problem for Fourth Powers.' Annals of Math., Vol. 40, (1939), 731-747.
- ⁶ Vinogradoff: 'Einige allgemeine Primzahlsätze.' Trav. Inst. Math. de Tobilissi, 3 (1938), 35-67.

CORRIGENDA

	<i>For</i>	<i>Read</i>
P. 114, Ref. 1	Chemiker. Zeitung.	Chemiker Zeitung.
5	Zellstoff. U. Papier.	Zellstoff u. Papier.
16	Zeit. fur. Physik.	Zeit. für Physik.
17	Sintzungs berichte. Preuss Akad.	Sitzungsberichte, Preuss. Akad.
P. 123, Ref. 8	Zeit. Fur. Physik.	Zeit. für Physik.
P. 153, Ref. 1	Compt. rend. Association Francaise Pour l'avancement des sciences, 7 session	Compt. rend. de l'Association française pour l'avancement des sciences, 7 ^e session
4	Ansichten Uber organische chemir.	Ansichten über organische Chemie.
P. 159, Ref. 5	Monatsh.	Monatsch.
13	„	„
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